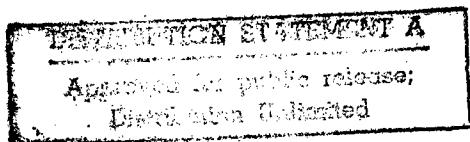


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USSR Report

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6 January 1984

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CHEMISTRY

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AEROSOLS

UDC: 541.182.2/3.18,057

ULTRASOUND INSTALLATION FOR PRODUCTION OF AEROSOLS (UZUA-3)

Moscow KOLLOIDNYY ZHURNAL in Russian Vol 45, No 5, Sep-Oct 83
(manuscript received 15 Mar 82) pp 998-1001

YES'KOVA-SOSKOVETS, L. S. and SARYCHEV, V. S., Institute of Biophysics,
USSR Ministry of Health, Moscow

[Abstract] A description is presented of a portable ultrasonic installation for production of aerosols, the UZUA-3. The device consists of a high frequency generator creating oscillations at the necessary frequency and an ultrasonic bath in which a type TSTS-19 piezoelectric element forms an ultrasonic fountain spray. The 800 KHz ultrasonic oscillator is based on two GU-29 vacuum tubes. The bath is made of organic glass and is a four-sided vessel with an aperture in the bottom in which the piezoceramic radiator is inserted. The rated output of the spray is 6 ml per minute generating aerosol particles with a mean diameter of 5 μm in an air flow of 3 1/3 cubic meters per second. Figures 3; references 2 (Russian).

[35-6508]

ANALYTICAL CHEMISTRY

UDC 543.257.1:543.8

IONOMETRIC DETERMINATION OF COPPER IN ORGANIC COMPOUNDS

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 38, No 9, Sep 83
(manuscript received 26 Mar 82) pp 1611-1616

DAVYDOVA, S. L., CHERVINA, L. V., SHPIGUN, L. K., RADCHENKO, A. F. and
ZARINSKIY, V. A., Institute of Petrochemical Synthesis imeni A. V. Topchiyev,
USSR Academy of Sciences, Institute of Geochemistry and Analytic Chemistry
imeni V. I. Vernadskiy, USSR Academy of Sciences, Moscow

[Abstract] A study is made of the possibility of using copper-selective electrodes for analysis of organic compounds of copper (salts of carboxylic acids and complexes of copper with organic ligands) by potentiometric titration. The experiment utilized fully solid phase copper selective electrodes of two types with membranes based on mixtures of silver sulfides with copper selenide or sulfide. The membrane potential of the copper-selective electrode was measured relative to a silver chloride electrode. The potentiometric titration curves are used to establish the optimal conditions of potentiometric determination of copper at concentrations to 0.04 µg/ml. Methods are developed for potentiometric determination of copper in copper-containing organic compounds of various compositions and structures both after preliminary mineralization by acids and directly in a water-ethanol solution. References 12: 3 Russian, 9 Western.

[38-6508]

UDC 543.253:546.18

INDIRECT POLAROGRAPHIC DETERMINATION OF PHOSPHORUS

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 38, No 9, Sep 83
(manuscript received 10 Aug 82) pp 1636-1639

KIRIYAK, L. G. and VATAMAN, I. I., Institute of Chemistry, Moldavian SSR
Academy of Sciences, Kishinev

[Abstract] A study is made of the indirect determination of phosphorus based on reduction of chlorate ions catalyzed by molybdate ions in the presence of an organic activator ligand--tartaric acid. The lower boundary of content which can be determined is 0.05 µg in 5 ml of solution. References 10: 6 Russian, 4 Western.

[38-6508]

UDC 543:546.92

ATOMIC-ABSORPTION DETERMINATION OF RUTHENIUM IN CATALYSTS

Moscow ZHURNAL ANALITICHESKOY KHMII in Russian Vol 38, No 9, Sep 83
(manuscript received 16 Aug 82) pp 1648-1651

IGOSHINA, E. V. and TALALAYEV, B. M.

[Abstract] The purpose of this work was creation of an atomic absorption method for determining ruthenium in the 4-40% concentration range in various catalysts based on oxides of aluminum and iron with relative standard deviation 0.04. Permissible values of relative standard deviations of ruthenium content in the preparation of catalysts of this type are at the level of 0.1. The work was performed on an atomic absorption spectrometer Varian AA-175 using a lamp with a hollow cathode manufactured by the same firm. Results of a check of the method by analyzing a known quantity of ruthenium are presented. The sample is first melted with a mixture of sodium peroxide and caustic soda. Relative standard deviation is found to be 0.03-0.04. The characteristic concentration of ruthenium is 2 μ g/ml. References 7 (Russian).
[38-6508]

UDC 543.544:546.593

PATTERNS OF ADSORPTION OF GOLD(III) BY NITROGEN-CONTAINING CHEMICALLY MODIFIED SILICAS

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 271, No 3, Jul 83
(manuscript received 29 Dec 82) pp 627-629

ALIMARIN, I. P., academician, NESTERENKO, P. N. and IVANOV, V. M., Moscow State University imeni M. V. Lomonosov

[Abstract] Adsorbents based on "Silokhrom C-120" silica containing chemically modified organic molecules with amino-, ethylene-, diamino-, diethylenetriamino-, tetraethylene-, pentamino- and trimethylammonium functional groups were studied. The dependence of adsorption of a chloride complex of gold (III) on the acidity of solutions studied in dynamic and static regimes was determined by the use of radioactive indicators, isotopes of ^{195}Au and ^{198}Au . The study marked the first time that a system was compiled in which the adsorption behavior of gold (III) and the form of dependence of its adsorption on the acidity of the medium reflect the ionic state of gold (III) in aqueous solutions and the interaction of its complex anions with polyamines. It was found that nitrogen-containing, chemically modified silica shows promise for use in concentrating trace elements of gold and in separating gold from excesses of non-ferrous metals. The advantage of silica as a mineral base is that it may be used in hybrid methods of determining gold which includes chemically modified silicas and its subsequent determination by neutron-activated, radiofluorescent, emission spectral analysis. The unusual adsorption of gold and the shape of

the adsorption curves as a function of the pH of solutions make it possible to identify the ionic state of gold in solutions. Figures 2; references 6:
2 Russian, 4 Western.
[12-2791]

UDC 547.898

STUDY OF EXTRACTIVE AND ION-SELECTIVE PROPERTIES OF MACROCYCLIC LACTONES

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 271, No 3, Jul 83
(manuscript received 27 Dec 82) pp 630-632

BOGATSKIY, A. V., academician, UkrSSR Academy of Sciences, LUK'YANENKO, N. G., POPKOV, Yu. A., NAZAROVA, N. Yu., MAMINA, M. U. and CHERNOTKACH, Z. A., Physico-Chemical Institute, UkrSSR Academy of Sciences, Odessa

[Abstract] Complex-forming and ion-selective properties of macrocyclic tri-lactones (I-IV) were studied. The complex-forming capacity of these compounds was studied by extracting picrates of alkaline and alkaline-earth metals from the aqueous phase in chloroform. It was found that macrocyclic lactones I-IV are weaker extractants than 18-crown-6 because of the presence of ester groups in their structure. The polyethyleneglycol fragment plays the decisive role in the complex-forming capacity of these compounds. Analysis of coefficients of selectivity showed that the macrocyclic lactones I-IV interact more effectively with cations of alkaline metals in the series of which they display significant potassium selectivity. Change of polarity of the liquid membrane affected cation selectivity of the macrocyclic lactones, especially for small rings. References 9: 4 Russian, 5 Western.

[12-2791]

UDC 551.311.8+553.981+550.48

FIRST RESULTS OF THE STUDY OF HYDROGEN ISOTOPIC COMPOSITION OF METHANE IN GASES OF AZERBAIJAN AND TURKMENIAN MUD VOLCANOES

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 271, No 3, Jul 83
(manuscript received 25 Jan 83) pp 715-717

YEROKHIN, V. Ye. and TITKOV, G. A., Geological Institute, USSR Academy of Sciences, Moscow (Presented by academician A. V. Pevye 24 Jan 83)

[Abstract] Results of a study of hydrogen isotopic composition in gases of 14 mud volcanoes in Azerbaijan and four in Turkmenia are discussed. It was found that the chemical composition of the mud volcano gases closely resembles that of deep layers of a sedimentary cross section. There was an inter-relationship of genesis of volcano gases and generation of petroleum hydrocarbons which provides important evidence concerning the oil-bearing prospects of deep layers of a sedimentary cross section of mud volcano regions in

Azerbaijan and Turkmenia. Data obtained concerning the isotopic composition of hydrogen of methane conform to ideas concerning the deep genesis of hydrocarbons in the aspect of deep amagmatic degassing of the earth. The isotopic composition of hydrogen of the mud volcano gases was similar to that of gases of oil and gas deposits but not to that of gases of magmatic volcanoes, fumaroles or hydrotherms. Figures 2; references 5: 3 Russian, 2 Western [12-2791]

CATALYSIS

CONFERENCE ON CATALYTIC PROCESSES HELD

Alma-Ata KAZAKHSTANSKAYA PRAVDA in Russian 22 Sep 83 p 3

[Text] On 21 September the All-Union Conference on Catalytic Reactions in the Liquid Phase opened in Alma-Ata. In addition to representatives from many scientific institutions, participants included directors of large industrial enterprises, associates from the republic's VUZes, and scientists from Bulgaria, the GDR, Hungary, Vietnam, and Czechoslovakia.

Contemporary industry would be inconceivable without catalytic processes. A ton of a catalyst (a substance that accelerates chemical reactions) helps produce more than 100 tons of a valuable chemical raw material. The synthesis of ammonia; processing of petroleum products; the production of polymers, fats, and medicines; and biochemistry are all inconceivable without catalysts. The volume of catalytic production is very high and in terms of tonnage, it exceeds many major sectors of industry.

At the center of attention at the conference are questions involving the use of coal resources, synthesis of plastics with prescribed properties, creation of long-lasting catalysts, and more.

9967
CSO: 1841/14

UDC 66.097.3:546.92.621

INFLUENCE OF ALKALI METALS ON PROPERTIES OF ALUMINOPLATINUM CATALYSTS IN
DEHYDROGENATION OF n-DODECANE

Leningrad ZHURNAL PRIKLADNOY KHMII in Russian Vol 56, No 9, Sep 83
(manuscript received 27 Jul 82) pp 2114-2119

MOROZ, A. M., KOGAN, S. B. and BURSIAN, N. R., All-Union Scientific Research Institute of Petrochemical Processes

[Abstract] A study is made of the influence of the addition of lithium, potassium and cesium on the catalytic properties of alumino-platinum catalysts under the conditions for dehydrogenation of n-dodecane at atmospheric pressure. The catalysts were prepared by successive saturation of a heated carrier with an aqueous solution of platinohydrochloric acid with subsequent drying and calcining, followed by an aqueous solution of an alkali metal nitrate, also with subsequent drying and heating. The catalysts were dried at 323, 383 and 403°K, 3 hours at each temperature. Calcining was performed at 773°K in air for 2 hours. The catalysts were tested in a laboratory dehydrogenation installation at atmospheric pressure, 753°K, molar $H_2 : C_{12}H_{26}$ ratio 8:1. The reaction products were analyzed by gas-liquid chromatography. The results showed that the content of monoolefins in the catalysts depended on the contact time. They indicate a decrease in the reaction rate of dehydrogenation of n-dodecane when alkali elements are introduced to the aluminoplatinum catalyst as a result of the decrease in dispersion of platinum on the surface of the carrier. The specific activity of the platinum remains constant. Positive results of alkali metals reported earlier are found to consist of suppression of secondary reactions such as cracking, skeleton isomerization and coke formation. The selectivity of the aluminum-platinum catalyst for dehydrogenation of n-dodecane is thus increased. Figures 4; references 10: 9 Russian, 1 Western.

[37-6508]

8

UDC 542.941.7

LIQUID PHASE HYDROGENATION OF ACETYLENE IN PYROGAS IN PRESENCE OF HETEROGENEOUS CATALYSTS AT ATMOSPHERIC PRESSURE

Leningrad ZHURNAL PRIKLADNOY KHMII in Russian Vol 56, No 9, Sep 83
(manuscript received 6 Jan 82) pp 2119-2123

MEN'SHCHIKOV, V. A., FAL'KOVICH, Yu. G. and AEROV, M. E.

[Abstract] The authors suggest hydrogenation of impurities in pyrogas in liquid phase in the presence of a solid phase catalyst. Studies were performed in the laboratory on artificial mixtures imitating pyrogas in terms of content of hydrogen, ethylene and acetylene. The remaining components were replaced by methane or nitrogen. Some experiments were performed on ethane pyrolysis gas. Non-noble metal catalysts such as aluminum-nickel-chromium, nickel on kieselguhr and cobalt-molybdenum were tested first. Studies were performed at 120-180°C using dodecane as the liquid phase. Palladium catalysts on various carriers were next tested. Acetone, dimethylformamide, alcohols, esters and water were tested as the liquid phase. The productivity of catalysts in hydrogenation of acetylene in real pyrogas at atmospheric pressure is approximately 1/20 as great as in the artificial mixtures. This is a result of the presence of other compounds. The studies showed that hydrogenation of acetylene in pyrogas up to a content of 0.0001 vol.% can be performed at temperatures of about 30°. Figures 3; references 3: 1 Russian, 2 Western.
[37-6508]

UDC 541.128.13:12.034:547.724:941.7

INFLUENCE OF HYDROGEN PRESSURE ON RATE AND MECHANISM OF HYDROGENATION OF DIFURFURYLIDENE ACETONE ON SKELETAL NICKEL TITANIUM ALUMINUM CATALYST

Leningrad ZHURNAL PRIKLADNOY KHMII in Russian Vol 56, No 9, Sep 83
(manuscript received 20 Oct 82) pp 2123-2126

MAT'YAKUBOV, R., ABDUGANIYEV, Ye. G. and KOZHEVNIKOV, V. S.

[Abstract] Studies made of the influence of hydrogen pressure on the rate and mechanism of hydrogenation of difurfurylidene acetone (I) on a skeletal nickel-titanium-aluminum catalyst. Comparison of kinetic curves of hydrogenation of (I) dienone under hydrogen pressure with results obtained at atmospheric pressure showed that they differ sharply. The formation of the intermediate enone at atmospheric pressure reaches 35-65% of the maximum, whereas under hydrogen pressure of 60 atm. the quantity of 1, 5-difurylpentene-1-one-3 (II) is not over 5 to 15% of the total mass of hydrogenated products. In the 20-80 atm. pressure interval, (I) is hydrogenated in a first order reaction, at 80-120 atm. --a zero order reaction. References 5 (Russian).
[37-6508]

UDC 66.095.1:66.097

CATALYTIC OXYETHYLATION OF LIQUID AMMONIA IN PRESENCE OF CATIONITE
WOFATITE KPS

Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 56, No 9, Sep 83
(manuscript received 8 Jul 81) pp 1966-1971

STOYANOV, A. D., BOYEVA, R. S. and KOTOV, St. V., Higher Institute of Chemical Technology imeni A. Zlatarovya, Burgas, Bulgaria

[Abstract] The purpose of this work was to establish some of the kinetic regularities characterizing heterogeneous catalytic oxyethylation of liquid (anhydrous) ammonia in the presence of a strong acid cationite, wofatite KPS, in the hydrogen form. Wofatite KPS from East Germany is a sulfurated copolymer of styrene and divinylbenzene containing 8% divinylbenzene. Experiments were performed in a laboratory steel autoclave 200 cm³ in volume equipped with separate dosing devices for ammonia and ethylene oxide and an electromagnetic stirrer. The reagents were introduced to the autoclave under a nitrogen pressure of about 5.9 MPa to allow the process to be conducted in the liquid phase. Kinetics studies were performed in the 40-80°C temperature interval with initial ethylene oxide concentrations of 0.672-3.225 mol·l⁻¹, molar ammonia to ethylene oxide ratios of 57.5-10.2 and catalyst concentration $2.9 \cdot 10^1$ g·ion·l⁻¹. The initial event in the catalytic interaction was found to be not protonation of the ethylene oxide molecule, but rather conversion of the cationite to the ammonia form. This is followed by a stage defining the reaction rate, simultaneous protonation of the oxygen atom with the active form of the catalyst and nucleophilic attack of the ammonia on the carbon atom of the activated ethylene oxide molecule. Figures 4; references 5: 2 Russian, 3 Western.

[37-6508]

UDC 66.097.3

OPTIMAL DISTRIBUTION OF ACTIVE COMPONENT IN CUPRIC OXIDE CRUST FINAL COMBUSTION CATALYST

Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 56, No 9, Sep 83
(manuscript received 16 Dec 81) pp 1971-1974

KAS'YANOVA, L. N., LUGOVSKOY, V. I., STAROSTINA, T. G. and TSYRUL'NIKOV, P. G.

[Abstract] The purpose of this work was determination of the optimal distribution of the active component in the catalyst IK-12-3 as a function of the conditions of performance of the process of catalytic decontamination of exhaust gases, on the example of the model reaction of oxidation of hydrogen. Studies were performed for a hydrogen concentration in the initial mixture of 0.5-2%, mixture temperature 200-400°C, catalyst grain diameter 6 mm, thickness of active crust 0.2-1 mm. Determination of the optimal active crust was performed by determining the parameters of a kinetic model, calculating the

process on an individual catalyst grain and construction of a model of the observed rates for grains with various active zone thicknesses. Analysis of temperature and concentration fields in the catalyst layer was used to determine the optimal thickness of the crust and its content of cupric oxide. The results produced indicate that, for IK-12-3 crust catalyst, the contact time necessary to achieve the required degree of conversion is less than when IK-12-1 catalyst is used with 2.5 times greater total CuO content. As the active zone thickness increases, contact time continues to decrease to a thickness of 0.6 mm (CuO content 20% in the crust). Further increases in active zone thickness lead to no further significant change in contact time. For a crust containing 15% CuO, the maximum active zone thickness is 1 mm, beyond which contact time does not further increase. Figures 2; references 6 (Russian).
[37-6508]

UDC 66.097.3:546.92'62:543.422.4

STUDY OF ALUMINOPLATINUM CATALYST MODIFIED BY ADDITION OF ALKALI ELEMENTS BY IR SPECTROSCOPY AND EPR METHODS

Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 56, No 9, Sep 83
(manuscript received 27 Jul 82) pp 1975-1977

KOGAN, S. B., MOROZ, A. M., ORANSKAYA, O. M., SEMENSKAYA, I. V.,
GORODETSKAYA, I. V. and BURSIAN, N. R., All-Union Scientific Research
Institute of Petrochemical Processes

[Abstract] The effect of alkaline additives to metal and acid centers of an aluminoplatinum catalyst is studied by IR spectroscopy of the absorbed carbon monoxide and EPR. The data produced indicate a change in the electron state of the platinum on the carrier in the presence of the alkali metals. The explanation suggested for the effect of addition of alkali metals is based on weakening of the electron interaction between platinum and alumina as a result of neutralization of acid centers of the carrier. It is shown that the introduction of alkali metals increases adsorption of carbon monoxide on platinum, changing the distribution of adsorption centers. Figure 1;
references 16 (Russian).

[37-6508]

UDC 541.123.3:66.097.3

INFLUENCE OF PREPARATION CONDITIONS ON PHASE COMPOSITION AND MACROSTRUCTURE OF ALUMINUM-MOLYBDENUM-CHROMIUM CATALYSTS

Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 56, No 9, Sep 83
(manuscript received 3 Nov 81) pp 1977-1983

EL'BERT, E. I., FRIDMAN, V. Z., PETROV, I. Ya. and TRYASUNOV, B. G.,
Kuznets Basin Polytechnic Institute

[Abstract] A study is made of an aluminum-molybdenum-chromium catalyst suggested earlier for the reaction of dehydrogenation of ethyltoluenes in

vinyltoluenes, containing 15 mass % Cr_2O_3 , 13 mass % MoO_3 and 72 mass % Al_2O_3 . The catalyst was prepared by successive saturation of $\gamma\text{-Al}_2\text{O}_3$ with ammonium molybdate tetrahydrate and ammonium dichromate. Experiments indicate that in the process of preparation of the catalyst, regardless of sequence of application of the components and conditions of heating, the catalyst synthesized consists of spinel (solid solution of chromium (III) oxide in $\gamma\text{-Al}_2\text{O}_3$), chromium and aluminum molybdate and corundum $\alpha\text{-Cr}_2\text{O}_3$ phases. The change in macrostructure upon heating in air is independent of the sequence of application of the components. Air and steam treatment helps to change the macrostructure of both binary and trinary mixtures based on $\gamma\text{-Al}_2\text{O}_3$ containing MoO_3 . The strong influence of the air-steam treatment on the macrostructure of aluminum oxide systems containing MoO_3 can be explained by the fact that at high temperatures and high partial pressures of water vapor MoO_3 may be converted to a more volatile and therefore more mobile form $\text{MoO}_2(\text{OH})_2$. Figures 3; references 17: 13 Russian, 4 Western.
[37-6508]

UDC 542.97:547.313.4

ISOBUTYLENE OLIGOMERIZATION ON OXIDES, PART 3: CATALYTIC PROPERTIES OF ALUMINUM/RHENIUM CATALYSTS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHMICHESKAYA in Russian No 9, Sep 83 (manuscript received 6 Aug 82) pp 2000-2002

KHODAKOV, Yu. S., ANDERS, K., NAKHSHUNOV, V. S., FELDHAUS, R., SUBBOTIN, A. N., NOVAK, Z. and MINACHEV, Kh. M., Institute of Organic Chemistry imeni N. D. Zelinskiy, USSR Academy of Sciences, Moscow; Central Institute of Organic Chemistry, GDR Academy of Sciences, Leipzig

[Abstract] Studies were conducted on the effectiveness of rhenium oxides and aluminum/rhenium oxides as catalysts in the oligomerization of isobutylene at 50 to 300°C. Testing of the rhenium oxides (ReO_2 , ReO_3 , Re_2O_7) and the aluminum/rhenium oxides (5-40% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$) showed that highest catalytic activity was obtained with Re_2O_7 calcined at 400°C in air. Treatment with nitrogen reduced activity by 20% and hydrogen inactivated the catalyst. Treatment with air following nitrogen or hydrogen resulted in recovery of activity. Since Re_2O_7 is the most acid oxide, oligomerization can be regarded as involving an acid mechanism. Figures 1; references 7: 3 Russian, 4 Western.
[28-12172]

UDC 542.97:547.212

ETHANE AROMATIZATION ON METALLOZEOLITE CATALYSTS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHMICHESKAYA in Russian
No 9, Sep 83 (manuscript received 12 Nov 82) pp 2002-2009

BRAGIN, O. V., VASINA, T. V., ISAKOV, Ya. I., PALISHKINA, N. V.,
PREOBRAZHENSKIY, A. V., NEFEDOV, B. K. and MINACHEV, Kh. M., Institute of
Organic Chemistry imeni N. D. Zelinskiy, USSR Academy of Sciences, Moscow

[Abstract] The effectiveness of zeolite TsVM and its metallozeolite congeners (M/H-TsVM, M = metal) in aromatization of ethane and ethylene at 400-600°C was evaluated in relation to the metal component and acidity. In the case of ethylene, the yield of aromatic hydrocarbons at 500°C approached 75% with H-TsVM; the activity of the catalysts increased in the following sequence which also reflected their acidity ranking: Na-TsVM << HNa-TsVM < H-TsVM. In addition, HNa-TsVM and H-TsVM were also active in the aromatization of ethane. Introduction of dehydrogenating components into H-TsVM, particularly platinum, increased the yield of aromatic hydrocarbons from ethane to 20% (a 1.5-2-fold increase). The activity of the zeolites in catalyzing aromatization of ethane was markedly improved by pretreatment of the bifunctional catalysts (Pt/H-TsVM, Pd/H-TsVM, Rh/H-TsVM) at 500-550°C in air, hydrogen, or air/hydrogen mixture. Furthermore, certain M/H-TsVM catalysts showed enhancement of catalytic activity in the aromatization of ethylene and ethane 2 or 3 h into the process, which was particularly noticeable with the Pt and Pd catalysts pretreated at 550°C in air or air and hydrogen. Figures 2; references 10:
5 Russian, 5 Western.

[28-12172]

UDC 542.97:547.313.4

TRANSFORMATION OF ISOBUTYLENE ON DECATIONIZED SUPER-HIGH SILICON ZEOLITE DOPED WITH VANADIUM

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHMICHESKAYA in Russian No 9,
Sep 83 (manuscript received 16 Nov 82) pp 2009-2014

KONDRAT'YEV, D. A., BOROVINSKAYA, T. B., DERGACHEV, A. A., DMITRIYEV, R. V.,
NEFEDOV, B. K., ALEKSEYEVA, T. V. and MINACHEV, Kh. M., Institute of Organic
Chemistry imeni N. D. Zelinskiy, USSR Academy of Sciences, Moscow

[Abstract] The extent of isobutylene transformation at 320 and 500°C with super-high silicon decationized zeolite (H-SVKTs) doped with various concentrations of vanadium was evaluated with respect to the vanadium content. At both temperatures with and without V, gaseous olefins and paraffins (C_2-C_5) are produced, as well as aliphatic and aromatic hydrocarbons (C_6-C_{10}).

Addition of V to a 0.3% content increased the total yield of aromatic hydrocarbons 1.5-fold at 320°C, and to a lesser degree at 500°C. At 320°C with 2.8 and 5.7% V in H-SVKTs the concentration of p-xylene accounts for ca.

60% of the products, while at 500°C with 0, 2.8, and 5.7% V the C₈ alkyl benzene fraction consists of 18, 34, and 40% p-xylene, respectively. Figures 4; references 10: 7 Russian, 3 Western.
[28-12172]

UDC 541.128.1

EFFECTS OF pH AND MODIFIER ON ENANTIOSELECTIVE HYDROGENATION OF ETHYL ACETOACETATE ON COPPER-NICKEL CATALYSTS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHMICHESKAYA in Russian No 9, Sep 83 (manuscript received 6 Dec 82) pp 2023-2026

CHERNYSHEVA, V. V. and KLABUNOVSKIY, Ye. I., Institute of Organic Chemistry imeni N. D. Zelinskiy, USSR Academy of Sciences, Moscow

[Abstract] The effectiveness of Cu/Ni catalysts in enantioselective hydrogenation of ethyl acetoacetate (EAA) was studied in relation to catalyst modification by tartaric acid and amino acids and the pH of modification. Significant differences were observed in the surface chiral complexes formed during modification of Cu/Ni catalysts by tartaric acid and S-alpha-amino acids at various values of pH. Asymmetry in hydrogenation of EAA on the Cu/Ni catalysts in question was largely due to the Ni component, and such enantioselective hydrogenation becomes apparent when the Ni concentration reaches 10-15 mass%. Figures 2; references 12: 6 Russian, 6 Western.

[28-12172]

UDC 541.128:542.91:547.21

PROPERTIES OF Co-Al₂O₃ CATALYSTS IN HYDROCARBON SYNTHESIS FROM CO AND H₂

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHMICHESKAYA in Russian No 9, Sep 83 (manuscript received 25 Nov 82) pp 2026-2029

KHOANG CHONG IYEM, KRYLOVA, A. Yu., SALEKHUDDIN, S. M., and LAPIDUS, A. L., Institute of Organic Chemistry imeni N. D. Zelinskiy, USSR Academy of Sciences, Moscow

[Abstract] Effective cobalt catalysts were prepared for Fischer-Tropsch synthesis by transmutation of gamma-Al₂O₃ with aqueous Co(NO₃)₂ and subsequent drying and firing at 450°C under air. Addition of B₂O₃ promoter to the Co-Al₂O₃ catalyst results in the production of hydrocarbons in which the olefin fraction is increased three-fold and the normal paraffin fraction is decreased ca. 1.5-fold. In addition, presence of B₂O₃ (0.5%) virtually abolishes polymerization, in that formation of hydrocarbons with more than 15 carbon atoms is practically nil. Addition of 1% acetylene to the synthesis gas has no effect on the overall hydrocarbon yield but increases CH₄ production to 55%. Figures 1; references 4 (Russian).

[28-12172]

CHEMICAL INDUSTRY

SHIPMENT OF CHEMICAL PLANT EQUIPMENT DESCRIBED

Moscow SOVETSKAYA ROSSIYA in Russian 28 Jun 83 p 1

[Text] Gorkiy Oblast, 28 Jun (TASS) -- Two steel giants have before them an odyssey through many rivers and seas; the towing of the gigantic equipment started yesterday on the Oka river. From the port of the Dzerzhinsk Chemical Machine Building Plant the ship "Ozernyy-210" and the steamship "Aldan" left pulling an unusual raft consisting of two huge industrial columns. The weight of each is 600 tons and they are over 90 meters long. They are destined for the Tobolsk Petrochemical Complex.

This trip from Europe to Asia will take over two months, using numerous waterways. According to experts' estimates, this transport operation will cost 2 million rubles. This is considerably cheaper than sending the columns unassembled. Shipping the columns unassembled would take at least a month, but the second assembly and adjustment of the equipment would require another 2 years. Now only a week is needed to install the columns.

9967
CSO: 1841/14

INCREASED USE OF SYNTHETIC CHEMICALS IN PRODUCTION

Moscow EKONOMICHESKAYA GAZETA in Russian No 40, Oct 83 p 1, 2

[Text] Chemicalization, or the increased use of chemicals in production, is one of the most important directions of scientific and technical progress. The production of mineral fertilizers and polymer materials and products of petroleum refining are what is known as large-scale chemistry. Small-scale chemistry is also being developed; it provides industry with various types of additive products and it helps intensify production and increase product quality.

The use of products from small-scale chemistry has a major economic impact on consumers since it opens up the possibility of producing a wide range of materials with prescribed properties. The immense national economic significance of these products was emphasized at the June (1983) Plenum of the CPSU Central Committee.

One of the scientific and technical programs in the 11th Five-Year Plan is devoted to the creation and incorporation of new processes of small-scale chemistry.

The implementation of this program is described in the review presented below. It was prepared by the Chemistry Department of the USSR State Committee for Science and Technology.

The total volume of production in the chemical and petrochemical industries has grown since 1970. If the 1970 level is taken as a baseline, in 1980 the volume increased by a factor of 2.2; in 1982 the volume increased by a factor of 2.4 over the 1970 level; and in 1985 the plan is to increase the volume by a factor of 2.8 over the 1970 level.

Review--Products with Prescribed Properties

The 26th CPSU Congress set the goal of increasing the output of small-scale chemistry products. It was pointing industry toward more complete fulfillment of the national economic demand for chemical additives for polymer materials and the synthesis of medicines, and for textile auxiliary materials, preservatives, catalysts, and reagents.

Included in the products of small-scale chemistry are materials produced in relatively small quantities--from several grams to tens of thousands of tons per year. They are of great importance in any case.

Small-scale chemistry products regulate quality, duration of service, and the direction of action of polymer and textile materials; they create a raw materials base for medicinal preparations; they increase the extraction of minerals; they increase the reliability and sensitivity and decrease the size of various types of electronic instruments used in domestic and technical settings; and they raise the technical level of scientific and medical research. The use of these additives opens up broad possibilities for creating materials with prescribed properties.

The assortment of small-scale chemistry products includes almost 20,000 different types of products. The demands of scientific and technical progress are constantly presenting new tasks in expanding and changing the list of products. In this connection it is very important that industrial production be flexible and easily changed. These characteristics were taken into account in the special comprehensive scientific and technical program called "Creation and incorporation of new processes for producing small-scale chemistry products, that will provide a substantial increase in the materials' technical properties and an improvement in their quality".

An 11-Fold Yield

Within the framework of the program, problems are resolved that involve the creation of new:

- dyes and textile auxiliary materials for light industry;
- motion picture film and photographic materials;
- materials with a high degree of purity for electronics, medical, and scientific research and analytic monitoring;
- chemical additives for sectors of industry working with polymers;
- surface-active substances for washing materials and petroleum extraction.

The economic effectiveness of the program can be judged by the following preliminary estimates. Almost all the expenditures on scientific research operations over the course of the entire five-year plan will be recovered in 1985; that is, at the very beginning of their incorporation. It is expected that every ruble invested for scientific purposes in this program between 1981 and 1985 will yield about 11 rubles in the future.

The capital investments made for the production of new small-scale chemistry products are also very effective. Estimates show that all the capital investments planned for the 11th Five-Year Plan will be recovered almost 1.8-fold when these products are introduced.

The development and assimilation into production of new types of dyes and textile auxiliary materials is an important part of the program. The fulfillment of this goal during the current five-year plan will contribute significantly to an improvement in the quality of consumer goods, and various textile products in particular. At present the domestic aniline dye industry

puts out about 500 different brands of dyes. The plan is to replace 30 percent of the product assortment with new products by 1985.

Of special interest is a unique class of dyes, the so-called vat-generated dyes. They take on their coloring form during the actual dyeing process. This gives the fabrics a special light and colorfastness against the effects of washing.

In 1983-1984 there are plans to develop industrial production of new brands of active dyes for natural fibers. At the Ivano-Frankovsk Fine Organic Synthesis Plant of the Ministry of the Chemical Industry, the equipment for this process has already been installed.

The "Soyuzanilprom" [Dyes and Organic Products Industry Association] (V. Alekseyev, chief) should be more actively involved in the technical refitting of its enterprises. There should be broader introduction of flexible, standardized mobile models for obtaining raw materials and semifinished products and there should be instrumental methods for quality control of the dyes.

Textile auxiliary materials make fabrics resistant to soil, grease, shrinkage, water, and wrinkling; and they make fabrics soft and provide them with anti-static properties. With these substances fabrics can be dyed more evenly, the process takes less time, and the durability of the dye is increased. One of the goals of the program is to create a progressive, domestic assortment of textile auxiliary materials.

In 1982, the Ivanovo "Khimprom" [Chemical Industry Association] initiated series production of a new preparation called "pirovateks" to be used for fireproofing fabrics. By 1985 this same enterprise will begin producing new textile auxiliary materials.

A separate sub-program is devoted to the creation and production of new motion picture photographic materials. It is well known that non-silver light sensitive materials are being used more and more in photographic and copying and duplicating technology. In addition to saving silver, this makes it possible to make copies and develop film rapidly; it also provides a high level of contrast and resolution capability, which is especially important in microfilm processes.

In accordance with the program, since the beginning of the five-year plan there has been industrial production of a number of electro-photographic materials based on the photo-conductivity of semiconductors and dielectrics; and part of the required control and measurement equipment has been developed.

The State Photochemical Industry Scientific Research and Design Institute, together with the Kazakh Technical Photography Scientific Research and Design Institute, has developed a process for a new color negative film for cinematography. In terms of quality and technical characteristics, it is on a par with the best film produced abroad. In 1985 the first industrial batch of this film should be produced and tested. The Kazan "Tasma" Industrial

Association has already produced over 40 percent of the units of the complex, multi-headed irrigating equipment for production of this film.

However, construction of the building for the machinery has not yet been started and the planned deadlines have been changed. The Ministry of the Chemical Industry (S. Golubkov, deputy minister) must take a critical approach to the state of affairs surrounding the realization of the goals of this sub-program.

A High Degree of Purity

Successes in contemporary electronics are tied to a significant degree to the output of small-scale chemistry products such as ferroelectrics. These materials can change their physical properties under the influence of an electrical or magnetic field. Use of these materials makes it possible to improve some of the most important indicators of electronics engineering: economy, speed, operational reliability, and miniaturization.

Since the beginning of the five-year plan, within the framework of the program Soviet scientists have developed a number of new ferroelectrics. Series production of these materials will begin in 1985. Fulfilling this goal will help raise the technical characteristics of color televisions, hydroacoustic devices and microcomputers to new levels.

Liquid crystals for technical use are being used more and more in instrument building, medicine, and everyday situations. The program devotes considerable attention to the creation of new types of these crystals. Goals for the development and production of thermo-indicator films for medicine on the basis of liquid crystals are being met successfully; so are the goals for production and delivery of liquid crystals with increased reliability and more rapid action to the electronics industry, to be used for various figure transparencies, wrist watches, and microcalculators.

Work is being done on the creation, production, and application of complexons; this is of great importance to many sectors of industry. The simplicity and ease of their synthesis, and the practically endless possibilities for modifying the structure of their molecules, open up broad prospects for designing compounds that will solve specific national economic problems. There are plans to develop production of complexons in Cheboksary by 1985.

With the use of compositions based on complexons, methods have been developed for washing thermal and electric power plants and State regional electric power stations before they are put into operation and during local operation. A method has been developed that reduces the number of washings to one-fifth of the previous number required. This anti-scaling composition allows normal operation of the circulation systems for cooling the condensers of the power stations for several years without changing the water, using a non-flushing system.

The use of complexons in oil drilling improves the operation of oil wells and intensifies considerably the industrial drilling processes. As a result of the high mineralization of water found at different drilling levels, salt deposits

form in the oil and gas wells. These deposits greatly reduce the oil yield. Complexons are active inhibitors of salt formations and mix well with the water found at the drilling levels; they do not clog the pores in the surrounding rock. Tests conducted at the "Orenburgneft'", "Perm'neft'", "Bashneft'", and "Tatneft'" Petroleum Associations have confirmed the high degree of effectiveness of these compositions.

Complexons have been used to create etching, desorbent, and modifying substances for the surface of semiconductor materials; production of these substances will start by the end of the five-year plan. They will be used in the electronics and watch-making industries and in the production of integrated microcircuits.

A variety of complexons have been developed for agriculture. A serious shortage of microelements in the soil leads to a decrease in the crop capacity and in a number of cases to plant diseases. Application of complexons makes it possible to provide plants with microelements in a biologically active, easily assimilated form; and some plant diseases can be cured, such as chlorosis. Tests conducted at various farms showed that with small doses of complexons (1-20 grams per plant), chlorosis can be cured completely and the crop yield increases. [microelements = trace elements]

Animals can also suffer from a shortage of microelements. Studies conducted in conjunction with the Fur Farming Scientific Research Institute helped in the development of a preparation based on complexons; production of this preparation has been developed at the Shostka Chemical Reagents Plant.

Biochemical Reagents

One of the most important problems in small-scale chemistry is the creation of a domestic assortment of biochemical reagents and highly purified preparations. The program provides for expansion of this list of products to include 1500 different varieties by 1985.

The "Biokhimreaktiv" [Biochemical Reagents] Scientific Production Association, together with the Far Eastern Scientific Center of the USSR Academy of Sciences, developed a complex process for obtaining biochemical preparations from non-edible marine raw materials and fish industry by-products. The AzSSR Academy of Sciences specializes in the problem of obtaining biochemical preparations from plants.

There are plans to put into operation in 1983 a system for obtaining a number of amino acids that are needed for medical purposes. The "Biokhimreaktiv" Scientific Production Association will be putting out five different enzymes by the end of the five-year plan; the use of these enzymes will enable physicians to diagnose in seconds the presence and severity of an infarct and to conduct mass epidemiological surveys of people and animals in very short periods of time.

The success of this important goal of the program depends to a great extent on the total specialization of "Biokhimreaktiv" in this particular area. Its

efforts are still scattered in different directions that are not related to the specific problem.

A characteristic element of technical progress is the broad utilization of synthetic polymer materials in all types of human activities. Although polymers have a number of valuable qualities, they also have a significant shortcoming. Heat, air, and light cause them to "age"; that is, they become brittle and they lose their elasticity and strength.

Special additives, called stabilizers, are used to avert this aging process. Other chemicals make it possible to change the polymers' properties and to give them new qualities. The application of these substances opens up prospects for using one polymer to obtain products with various practical properties.

The program outlines the development and production of a number of stabilizers, modifiers, accelerators, vulcanizing agents, and plastifiers. Non-staining and biologically inactive stabilizers are being introduced for polymer articles for public consumption and polymers that come into contact with food products.

A raw materials base has been created for developing the production of stabilizers on the basis of available phenol. Original processes have been developed for obtaining this raw material for a broad variety of agidol-type stabilizers that have a wide range of action.

"Agidol-1" not only protects polymers from aging, it is also an effective anti-oxidant additive for fodder which preserves the fodder's nutritive properties for a long period of time. "Agidol-40" protects polymers from aging, as well as cosmetics and medicinal preparations. The "agidol-2", "agidol-20", and "agidol-123" stabilizers have proved to be highly effective in many polymers and polymer compositions.

Tests have shown that the available phenol stabilizers, or agidols, are highly effective economically. Therefore, it is very important for the USSR Ministry of Petroleum Refining and Petrochemical Industry (A. Lukashov, deputy minister) to speed up industrial production of developments using phenol stabilizers and to accelerate the progress of work being done at the Sterlitamak Petrochemical Experimental Industrial Plant.

Responses to Previous Reviews Appearing in EKONOMICHESKAYA GAZETA

In response to the review "Engine Saves Fuel" (No 31):

"The material contained in the review is very timely. The possibility of reducing the expenditure of petroleum fuels and curbing air pollution today determines the future growth of the country's motor vehicle fleet.

"In 1983 the first engines for GAZ (Gorkiy Motor Vehicle Plant) trucks using a new operating system with a vortical motion charge were produced; the new system provides improved fuel economy--by 5-6 percent--and there is a 25 percent reduction in the exhaust's carbon monoxide content. Production of an economical engine with reduced toxicity for the "Volga" automobile has also

been organized. "Ozon" [Ozone] carburetors are being installed in the VAZ [Volga Motor Vehicle Plant] passenger cars; the carburetors have electronically controlled economizers for forced idling. These carburetors make it possible to reduce fuel consumption by 5 percent with a simultaneous decrease in the output of toxic substances. Models have been made and the finishing touches are being put on a new engine for the "Zaporozhets" car.

"The Ministry of the Automotive Industry has issued an order approving a progressive program for producing motor vehicles with microprocessor control systems; functions and responsibilities of the developing organizations have been defined; and a number of organizational measures have been implemented. Series production of modifications for passenger cars and trucks with microprocessor ignition control systems and the economizers for forced idling of gasoline engines is planned to start in 1984."

A. Titkov, chief of the Design and Experimental Work Administration of the Ministry of the Automotive Industry

"The review accurately reflects the problems that must be solved in the implementation of the program for creating and producing new types of internal combustion engines: fuel economy, adaptation to new types of fuel, and reduced toxicity of the exhaust gases. "Soyuznefteorgsintez" [Processing of Oil and Production of Organic Synthesis Products Industrial Association] is carrying out a number of studies on the rational utilization of petroleum products, on the development of future fuels based on gasoline and methanol blends, compositions of gasoline and methyltributyl ether (MTBE), and so on.

"At present the State Commission for Testing Fuels, Oils, and Special Liquids has approved the use of gasolines with MTBE in existing engine models."

V. Ryabov, chief of the Processing of Oil and Production of Organic Synthesis Products Industrial Association

In response to the review "Automation in Scientific Research and Design" (No 33):

"All the aspects of the review are of interest to scientific and design organizations of the Ministry of the Machine Tool and Tool Building Industry. The observations on the difficulties involved in introducing automated design systems are correct.

"The Ministry of the Machine Tool and Tool Building Industry supports the proposal expressed in the review that a State Algorithm and Program Base be created for automated design systems that will make it possible to reduce the amount of time needed to develop programs by making use of common system and invariant programs."

G. Boym, deputy chief of the Technical Administration of the Ministry of the Machine Tool and Tool Building Industry

UDC 66.628.543.002.237

IMPLEMENTATION OF DESIGN DECISIONS FOR WASTE-FREE TECHNOLOGICAL SYSTEMS AT
PERVOMAYSK CHEMICAL PLANT

Kiev KHMICHESKAYA TEKHNOLOGIYA in Russian No 5, Sep-Oct 83
(manuscript received 21 May 83) pp 18-21

KIYEVSKIY, M. I. and YEVSTRATOV, V. N.

[Abstract] The limited water resource availability and impossibility of dumping waste water into the densely populated surroundings have forced Pervomaysk chemical plant to implement a combined system of purification, reutilization and elimination of waste waters and production wastes, allowing complete elimination of dumping of all types of industrial and domestic waste waters, with maximum reutilization of production wastes. The combined system includes local water recycling with required purification for all major production sections, general plant structures and installations in which waste water is purified as necessary depending on the contaminants present for reuse in production, while the wastes formed are processed into commercial products. The major units of this system have been constructed and are in successful operation. In the production of chlorine and caustic soda by the diaphragm method, a local recycling plant has been in use since 1975, maintaining the salt content of recycled water at or below 10 g/l as sodium chloride, pH 11-12. A full biological purification plant for waste waters contaminated with organic impurities has been in use since 1973, achieving a BOD of purified waste water of not over 6-8 mg O₂/l. There is a system which operates plant-wide for collection of highly-mineralized waste water for desalination by distillation in a 7-section evaporator which was put on stream in January of 1982. The evaporator has a capacity of 500 m³/hr. The waste water is then neutralized by addition of hydrochloric acid or alkali and clarified by addition of a coagulant and filtration on high-speed quartz filters. Domestic waste water from the city as well as industrial waste water from the plant is passed through an installation for deep additional purification of biologically purified waste water. The method, involving adsorption of organic compounds on activated microporous anthracite and ion exchange adjustment of mineral composition, produces granulated nitrogen fertilizers as a byproduct.

[36-6508]

COMBUSTION

UDC 615.012/.014:614.833

DETERMINATION OF FIRE AND EXPLOSIVE PROPERTIES OF SOME AGENTS USED IN
PRODUCTION OF MEDICINES

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 17, No 8, Aug 83
(manuscript received 10 May 83) pp 989-992

KARABANOV, Yu. F. and CHASTUKHINA, M. I., Ivanovo Power Institute

[Abstract] Fire-hazard and explosion-hazard properties of 9 liquids and 11 powders used in medicine production were determined by analytical calculations and experimentally. The temperature and concentration limits of ignition were determined for vapors of the liquids and the lower concentration limit of ignition was found for the powders. Names and formulas of the substances and relevant parameters are tabulated and discussed. Figure 1;
references 4 (Russian).

[22-2791]

ELECTROCHEMISTRY

UDC 543.253

IONOSELECTIVE SOLID PHASE ELECTRODE SENSITIVE TO AMMONIUM IONS,
ELECTROCHEMICAL PROPERTIES

Moscow ELEKTROKHIMIYA in Russian Vol 19, No 9, Jun 83
(manuscript received 12 Nov 81) pp 1173-1177

VLASOV, Yu. G., MILOSHOVA, M. S., ANTONOV, P. P., EFA, A. Ya. and
BYCHKOV, Ye. A., Leningrad State University imeni A. A. Zhdanov

[Abstract] Experimental results were reported of the investigation of solid phase ion-selective electrodes (ISE) with heterogenic membranes $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$.
5.3 H₂O in aqueous and methanolic solutions. The membranes were obtained by copressing ammonium phosphomolybdate with polystyrene at 20-180°C and 400-600 MPa. These electrodes were shown to be sensitive to ammonium ions in the concentration range of 10⁻⁵ to 10 M NH₄NO₃. The solid phase electrodes were comparable to glass electrodes in respect to selectivity, but were less selective than film electrodes. They performed well both in water and in methanol solutions in a wide range of pH values. Figures 5; references 7: 5 Russian, 2 Western.

[21-7812]

UDC 541.138.2

RADIOCHEMICAL STUDY OF ANODE DISSOLUTION OF ORTA AT HIGH POSITIVE POTENTIALS,
AQUEOUS AND ALCOHOLIC SOLUTIONS

Moscow ELEKTROKHIMIYA in Russian Vol 19, No 9, Jun 83
(manuscript received 23 Apr 82) pp 1183-1187

MIRKIND, L. A., GORODETSKIY, V. V., AL'BERTINSKIY, G. L. and GORODETSKAYA, I. L.,
Scientific Research and Design State Institute of Lacquer-Dye Industry,
Moscow; Scientific Research Physical-Chemical Institute imeni L. Ya. Karpov,
Moscow

[Abstract] Oxidative ruthenium-titanium anodes (ORTA) are widely used in production of chlorine and chlorates. Corrosion rate of ORTA was determined by a radiochemical method by determining the dissolution rate of ruthenium in

organic or mineral electrolytes (aqueous and methanolic sulfate and perchlorate solutions and in adipic acid monomethyl ether solution). Small quantities of organic compounds inhibited corrosion rate of ORTA. In methanol, the corrosion rate did not exceed 10^{-6} gm.cm $^{-2}$.hr $^{-1}$, even at high positive potentials. Figures 4; references 13: 12 Russian, 1 Western.
[21-7813]

UDC 541.135.4

ELECTROLYTIC REDUCTION OF LEAD CHLORIDE DISPERSED IN POLYMER MATRIX

Moscow ELEKTROKHIMIYA in Russian Vol 19, No 9, Jun 83
(manuscript received 6 May 82) pp 1208-1211

LYAMINA, L. I., KURMASHOVA, I. A., TARASOVA, N. I. and GORBUNOVA, K. M., Institute of Physical Chemistry, USSR Academy of Sciences, Moscow

[Abstract] Experimental results were reported of a study of cathode reduction of lead chloride dispersed in isoprene-styrene thermoplastic (IST). Under conditions of complete encapsulation of $PbCl_2$ particles, the cathode reduction process provides for supply of electrons from the current source to $PbCl_2$ particles followed by removal of the reaction products (chlorine ions) through the polymer layer. The process is described by an autocatalytic curve characteristic of solid phase reactions. Microscopic evaluation of the process showed that the metal crystallized in form of dendrites. Addition of up to 25 vol-% of the polymer resulted in penetration of the dendrites through polymer layers. With a 42% of IST the reduced lead crystallized in form of spikes which did not penetrate the polymer capsule. Figures 5; references 5: 4 Russian, 1 Western.

[21-7813]

UDC 541.13

PORE DEVELOPMENT DURING REVERSIBLE ELECTRIC BREAKTHROUGH OF BI-LAYER LIPID MEMBRANES

Moscow ELEKTROKHIMIYA in Russian Vol 19, No 9, Jun 83
(manuscript received 12 May 82) pp 1218-1224

CHERNOGORODIK, L. V., SUKHAREV, S. I., KUSHNEV, V. V. and ABIDOR, I. G., Institute of Electrochemistry, USSR Academy of Sciences, Moscow

[Abstract] Experimental results were reported of the study of conductivity changes in bi-layer lipid membranes modified with UO_2^{2+} ions exposed to a double pulse of current. The kinetics of the development of reversible membrane breakthrough in mono and divalent ionic solutions was studied along with the effect of saccharose and hemoglobin on the conductivity during this breakthrough. The results obtained supported the assumption that a current increase

during reversible electric breakthrough is associated with increased number of pores, enlargement of their radii and consequently increased conductivity through these pores. Indeed a given conductivity may be achieved by a large number of small pores or a small number of large ones. Figures 4; references 14: 5 Russian, 9 Western (4 by Russian authors).

[21-7813]

UDC 541.135.5

SOLID CONTACT ION-SELECTIVE ELECTRODES BASED ON NEUTRAL COMPLEXING AGENTS

Moscow ELEKTROKHIMIYA in Russian Vol 19, No 9, Jun 83
(manuscript received 20 May 82) pp 1225-1230

STEFANOVA, O. K., ROZHDESTVENSKAYA, M. V. and GORSHKOVA, V. F., Leningrad State University imeni A. A. Zhdanov

[Abstract] The goal of the present study was to develop a stable solid contact electrode based on membranes with neutral carriers: valinomycin and macrotetralide with selective properties towards potassium and ammonium respectively. Various redox systems were utilized to stabilize the potential of internal current discharge: redoxite EO-7, GEM, and a cation exchange resin KU-2 in a mixed form of Fe^{2+} - Fe^{3+} . The study was limited to systems in which the reaction of the electrode to the oxidation potential occurred as a result of a change in the current discharge potential in respect to the membrane phase. It was assumed that redox systems had no effect on the membrane-solution interphase potential nor on the diffusion potential within the membrane. Experimental results were reported of the drift of this potential as a function of time, and the effect of the internal redox system on the potential. Figures 2; references 17: 10 Russian, 7 Western.

[21-7813]

FERTILIZERS

NEW FERTILIZER PLANT

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 2 Oct 83 p 2

[Article by L. Leont'yeva, SOTSIALISTICHESKAYA INDUSTRIYA correspondent:
"There Will Be More Fertilizer"]

[Text] The outstanding construction project in the kray has entered its final stage--the production of carbamide in Nevinnomysk, the city of chemists. This is the seventh stage of the largest fertilizer combine in the Northern Caucasus, the "Azot" [Nitrogen] Chemical Production Association.

There is already an enterprise operating within the "Azot" Association that has a carbamide production capacity of 270,000 tons per year. The enterprise was built according to an original model, which provides high product quality and labor productivity that is five times greater than at the existing enterprise.

The first 10,000 tons of carbamide will be produced ahead of schedule this year. Another 330,000 tons will be produced next year. Each kilogram of this fertilizer provides an additional 2-4 kilograms of produce during the harvest.

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CSO: 1841/14

PROBLEMS IN CONSTRUCTION OF AMMONIA PRODUCTION COMPLEX CITED

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 22 Sep 83 p 1

[Article by L. Ambinder, construction department chief of the newspaper KUZBASS: "Makeweight Beyond the Plan"]

[Text] One can say without exaggeration that today the attention of the entire oblast is fixed on the main construction site of the Kuzedeyev basin, the second complex for the production of ammonia in the Kemerovo "Azot" [Nitrogen] Association. Recently a sovkhoz director told me all about the merits of liquid ammonia, and the great results that come from applying it to fields. But as of now the association does not even have enough ammonia for its own industrial needs. Today chemists are reaping the fruits of the imbalance that was permitted in the development of capacities; this imbalance has been the focus of attention numerous times, including in the press. A number of enterprises are operating at half-strength, simply because there is not enough ammonia. Efforts to make up the deficit by receiving supplies from elsewhere are not solving the problem. In a six-month period alone the "Azot" Association workers fell short in their supply of ammonia by 100,000 tons. All hopes for restoring a normal production cycle are tied to the new, large-capacity unit that is being built and will produce 450,000 tons of the initial product annually.

The eight-month results are not a cause for optimism, however. The plan has been fulfilled by 83 percent, even though in August work valued at 1.6 million was completed.

V. Koptelov, general director of the "Azot" Association, said, "This was the same rate that we had in May."

In his opinion, there is a 2 and even 3 month lag behind schedule at one of the sectors. There is very little time remaining before the completion deadline. The amount of work that has still not been done is quite significant. But it is not clear exactly what type of work remains to be done. According to data from the Main Kuzedeyev Basin Construction Administration, additional work valued at 4.3 million rubles must be finished before the complex can be put into operation. This is a real goal, especially since a decision was made to combine construction and installation work with start-up and adjustment work. The problem is that work valued at 1 million plus rubles has accumulated in addition to the planned volume of work. The Kuzedeyev Basin Production

Mangagement Administration of the USSR Ministry of Installation and Special Construction Work estimates that there will be twice as much work of this nature. Similar planning costs, for which the customer is primarily responsible, are repeated with surprising regularity at each complex. They disrupt the organization of operations at the project: on the one hand, construction workers are approaching fulfillment of the plan in terms of rubles, but on the other hand the complex cannot be put into operation.

Also on the customer's conscience is lack of coordination in planning the power section.

A. Ivanov, chief engineer of the "Kemerovokhimstroy" [Kemerovo Chemical Construction] Trust, said, "The impression is that planners and operators are governed by different standards. Back in March we delivered a covered distributor unit for installation at one of the most important electric substations in the complex. Everyone was rushing us. Now the operators are claiming that the foundations have been designed incorrectly, that they are a half-meter too high. They need to be torn up."

The designers of the complex, the Kemerovo Branch of the State Nitrogen Industry and Products of Organic Synthesis Scientific Research and Design Institute (N. Reshetnikov, director) are proud that they were able to lighten the complex by 3000 tons. They made the complex 40,000 tons more powerful than its predecessor. This is even more reason why elementary errors are inexcusable.

The delivery of materials is a separate issue altogether. In September, 3 months before the complex is supposed to be put into operation, there is still talk about the status of various missing equipment.

V. Kulik, the association's deputy director for capital construction, tried to defend himself by saying, "We were forced to use our own resources to manufacture things that should have been supplied by plants of the Ministry of Chemical and Petroleum Machine Building together with the basic equipment. These were the so-called 'small items'. They turned out to be so major, though, that we had to ask for help from various enterprises in the city."

Now the Main Kuzedeyevo Basin Construction Administration and the oblast party organization are doing everything to step up the pace of work at the complex and to put it into operation by the end of the year. Socialist competition has been developed with a new intensity in all the sectors, and a great deal of work is being done to strengthen labor discipline. This inspires confidence that the difficulties that have arisen will be overcome. The other day the gas supply for the complex was completed. Next the boiler plant will be fired up, and the engineering plans for the operating cycle will be adjusted.

9967
CSO: 1841/14

STATE COMMITTEE REVIEWS PROGRESS IN FERTILIZER INDUSTRY

Moscow EKONOMICHESKAYA GAZETA in Russian No 42, Oct 83 pp 1-2

[Review prepared by the Chemistry Department of the USSR State Committee for Science and Technology: "Advances in Fertility Industry"]

[Text] In compliance with decisions of the 26th CPSU Congress and the country's Food Program for the 11th Five-Year Plan, the raw material base is being developed with the purpose of achieving fuller utilization of the capacities for producing mineral fertilizers and chemical additives. The plans are for increasing the mineral fertilizer production volume by almost a time and a half in the five-year plan. Latest achievements of science and technology are at the foundation of the major projects under way.

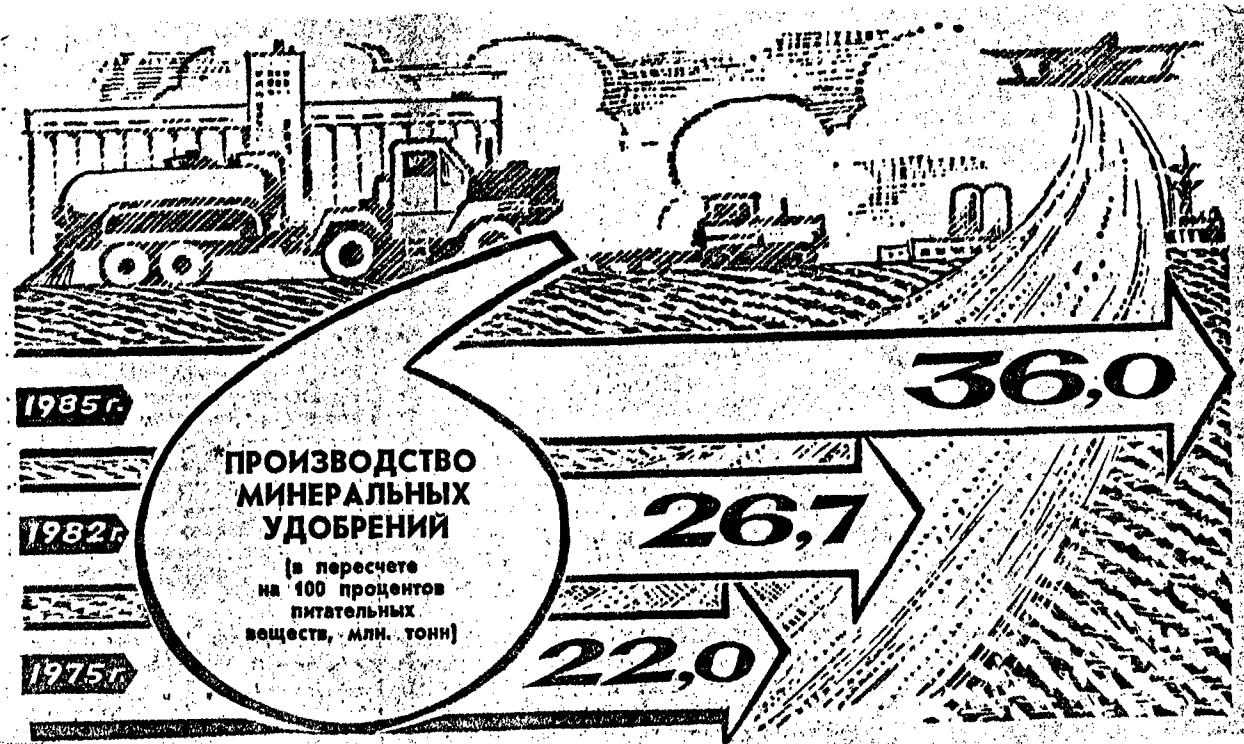
Expansion of chemical industry's raw material resources is the objective of scientific-technical programs described in the review below, prepared by the USSR State Committee for Science and Technology.

In compliance with the USSR Food Program, plans have been made for raising deliveries of mineral fertilizers to agriculture to 30-32 million tons (corrected for 100 percent nutrient content) in 1990. Measures have been determined for raising the quality of mineral fertilizers, expanding their assortment and increasing production of their most progressive forms.

The following scientific-technical programs are promoting reinforcement and development of the raw material base of fertility industry: "To Develop and Assimilate Production Processes and Equipment for the Acquisition of New Highly Concentrated and Long-Acting Mineral Fertilizers" and "To Develop and Assimilate New Production Processes for the Acquisition of the Most Important Multipurpose Inorganic Products Promoting Integrated Use of Raw Minerals."

Potassium and Phosphates

The Verkhnekamskoye potassium deposit in the Western Urals and the Soligorskoye potassium deposit in Belorussia will dependably serve the national economy for



*Mineral fertilizer production (corrected for 100 percent nutrients, million tons)

many long years to come. But at the same time, concentration of potassium fertilizer industry in essentially two locations has caused the arisal of a number of hard-to-solve problems.

The territory over which potassium fertilizers are used has expanded significantly. These fertilizers must now be applied even to the soils of the Central Asian republics, where until recently they enjoyed practically no use at all.

Assimilation of a new potassium ore deposit--Karlyukskoye in the Turkmen SSR--is becoming increasingly more urgent. Shaftless extraction by the method of underground leaching of sylvinitc is being laid at the basis of its development. This method eliminates heavy labor, significantly reduces salt dump formation and raises the labor productivity of potassium fertilizer production.

The scientific-technical program foresees the assignments of creating an experimental installation at the Karlyukskoye deposit for the purpose of developing progressive procedures for extracting potassium salts by the underground leaching method. However, the work is progressing extremely slowly. The Ministry of Mineral Fertilizer Production should turn attention to this problem. After all, it is today that the foundation of the powerful base for production of potassium fertilizers in the region is being laid.

Production of chlorine-free potassium fertilizers, which are needed so much for potatoes, flax, buckwheat, sunflower, tea, grapes, citrus and some other crops, is the bottleneck of potassium industry. For the moment such fertilizers are being produced in limited quantities, even though the demand for them is great.

The scientific-technical program calls for developing production of a chlorine-free potassium fertilizer--potassium nitrate--on an experimental industrial scale. But in the course of this assignment's fulfillment, difficulties were revealed in utilizing the byproduct chlorine gas that is formed in the process. Under these conditions organization of large-scale production of potassium sulfate was deemed to be the most suitable.

This year an industrial installation producing potassium sulfate with an annual output of 50,000 tons must be placed into operation in the "Beloruskaliy" Association. Sodium sulfate--a waste from the production of synthetic aliphatic acids--will be used as the raw material.

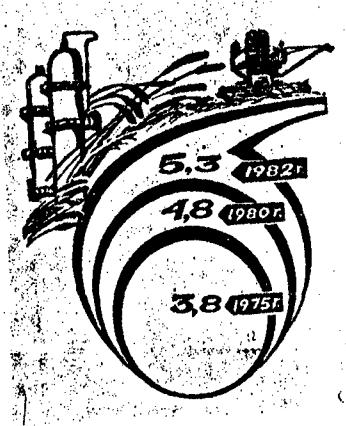
Among the materials provided to agriculture, phosphorus fertilizers are the scarcest. Our country's soils are phosphorus-poor for the most part. This is why the ratio of phosphorus pentoxide to nitrogen in the supplied mineral fertilizers must be 0.9. In fact, however, it is significantly lower, which reduces the effectiveness with which fertilizers are used.

In order that phosphate industry could be supplied with more of the raw material it needs, production of concentrate by the "Apatit" Production Association will be increased, and the highest practically possible production volume of the highest quality concentrate at the Khibinsk group of deposits will be achieved. There are plans for raising the proportion of the ores from the Karatau basin within the total balance of raw phosphate extracted in the country. But even this will not be enough. New sources must be assimilated right now.

Research and experiments are being conducted in accordance with the scientific-technical program to support preparation of low-grade phosphate ore deposits for industrial development. This includes the Oshurkovskoye, Beloziminskoye, and Seligdarskoye in Siberia, the Dzheroy-Syrdarinskoye in Uzbekistan and a number of others. The main thing here is to solve the problems of enriching the low-grade ore.

Unfortunately, the USSR Ministry of Nonferrous Metallurgy is clearly late in developing the complex Beloziminskoye deposit. Having placed an experimental factory into operation at the Oshurkovskoye deposit back in 1981, the Ministry of Mineral Fertilizer Production has still not provided the personnel it needs.

The assignments of the program include providing mining industry with highly selective flotation agents for enrichment of phosphate ore. Tests conducted in 1982 and 1983 on one such flotation agent at the "Apatit" Production Association demonstrated the possibility of extracting 1.5 percent more concentrate while simultaneously simplifying the procedures of a closed water recycling process. Use of the new reagent at this enterprise, the country's leading one, would make it possible to obtain about 300,000 tons of apatite concentrate per year.



Delivery of phosphate fertilizers to agriculture (corrected for 100 percent nutrient; millions of tons)

The Kovdor Mining and Concentration Combine of the USSR Ministry of Ferrous Metallurgy possesses even greater reserves for increasing production of apatite concentrate using progressive concentrating procedures and highly selective flotation agents. Extraction of apatite concentrate from the ores of the Kovdor Mining and Concentration Combine is below 60 percent. Were this indicator to be increased to at least 80 percent, about another 600,000 tons could be obtained per year without significant outlays.

The Ministry of Chemical Industry must organize production of highly selective flotation agents to support chemical mining industry and other sectors.

A Unique Deposit

The center of gravity of raw mineral extraction is gradually shifting eastward. In this connection the value of nature's storehouses located in the European part of the country is rising. Take as an example the deposit of natural bischofite in Volgograd Oblast or the Yaregskoye titanium ore deposit in the Komi ASSR. The assignments of preparing these unique deposits for industrial exploitation have been included in the scientific-technical program.

The Volgograd bischofite deposit was discovered in 1969 by oilmen. Its reserves are estimated at hundred of billions of tons. Moreover a ton of ore or a cubic meter of brine extracted by the underground bischofite leaching method contains more bromine than other raw material sources.

Volgograd bischofite may be used as a most effective raw material for the production of pure magnesium and bromine oxide, metallic magnesium and magnesium chlorate defoliant.

Refractory materials made from pure magnesium oxide serve steel casting operations three times longer. The quality of thermoelectric heating elements for domestic electric ranges can be sharply improved with minimum consumption of electric power.

Production of pure magnesium oxide out of Volgograd raw material by the method of thermal hydrolysis will result in a large quantity of hydrochloric acid, which could be used for the production of fertilizers and nutrient phosphates out of poor raw material.

Recently the Ministry of Petroleum Industry has appealed several times to the Ministry of Chemical Industry to organize deliveries of drilling mud to petroleum industry based on calcium bromide--a heavy liquid necessary for the drilling of wells encountering abnormally high reservoir pressure. Its use makes it possible to decrease drilling time, to reduce the accident rate and to make it easier to tap into a bed. Development of the Volgograd deposit would help to solve this problem.

As a result of research conducted recently, another promising area of application of crude magnesium chloride brines has taken shape--their use as effective tempering liquids in machine building, in place of scarce oils. The new liquids based on brines are not inferior to organic oils, and in relation to a number of indicators they are even superior to them. This was practically verified in Volgograd, Volgodonsk and Krasnodar. Temporarily, brine is being acquired from an exploratory well in the Narimanovskaya area near Volgograd.

Initiation of the development of the Volgograd bischofite deposit and organization, on its basis, of the production of pure magnesium and bromine oxide, phosphorus fertilizer and, in the future, metallic magnesium, chlorine and other products will produce a considerable national economic impact. Nonetheless, the Ministry of Chemical Industry is constantly postponing creation of an experimental industrial brine extraction operation in the Volgograd "Kaustik" Production Association, with the purpose of working out the procedures of extracting and integrated processing of raw material containing magnesium chloride and bromine.

It would be pertinent to recall that in 1982, First Deputy Minister of Chemical Industry L. Osipenko promised the State Committee for Science and Technology that the brine operation would begin production in the second quarter of 1983. But the discrepancy between word and deed remains.

At a Bureaucratic Boundary

A major problem requiring solution is production of titanium dioxide pigment, which enjoys broad use in paint and varnish industry, in pulp and paper industry, in the production of plastics and industrial rubber articles, and in other sectors. In terms of its qualitative indicators titanium dioxide is significantly superior to all other white pigments--lithopone, zinc white and white lead. However, the proportion of this highly important pigment is significantly lower at the moment than it should be. The national economy's demand for this progressive material is not being satisfied.

A sulfuric acid process is used to produce titanium pigment in the Soviet Union. It must be replaced by the chlorine method. The main advantages of it are the high quality of the resulting pigment and significant reduction of

toxic production wastes. We are aware of the difficulties enterprises producing titanium pigment in Sumy and in the Crimea experience due to these wastes.

The chlorine process is continuous and fully automated, while the sulfuric acid procedure is cyclic, and only certain stages are subjected to automation. Presence of the unique Yaregskoye titanium ore deposit, which produces ore suitable for production of titanium dioxide pigment by the chlorine method, opens up broad possibilities for introducing this progressive technology.

The Yaregskoye storehouse is the largest titanium deposit. The concentration of titanium dioxide in its ore is several times higher than in other places.

Strange as it may seem, Yarega remains essentially without a master. In the budget, the deposit is listed as belonging to the Ministry of Petroleum Industry, which is not at all interested in its development. The Ministry of Petroleum Industry has been building an experimental industrial mining and concentration complex since 1963. All deadlines foreseen by the assignments of previous scientific-technical programs and a number of government decrees have not been met.

By all rights the Yaregskoye deposit must have an interested master. In our opinion the Ministry of Chemical Industry would be the best of all for this role, since it is responsible for satisfying the national economy's demand for titanium oxide pigment. But the Ministry of Chemical Industry does not have miners: During the reorganization the entire miner staff was transferred to the Ministry of Mineral Fertilizer Production. This means that we need to create a subdivision in the Ministry of Chemical Industry which would be responsible for many of the raw mineral deposits.

Solution of these and other problems will make it possible to hasten scientific-technical progress in an important direction.

11004
CSO: 1841/15

INORGANIC COMPOUNDS

UDC 541.1:546.131-143

SPEED OF ULTRASOUND AND ADIABATIC COMPRESSIBILITY IN MELTED MIXTURES OF URANIUM TETRACHLORIDE WITH POTASSIUM CHLORIDE

Leningrad ZHURNAL PRIKLADNOY KHMII in Russian Vol 56, No 9, Sep 83
(manuscript received 30 Nov 81) pp 2152-2154

KUZNETSOV, Yu. S., KUREATOV, N. N., RASPOPIN, S. P., STRELOV, V. A. and CHERVINSKIY, Yu. F.

[Abstract] For the first time, the speed of ultrasound is measured in melted binary mixtures of uranium tetrachloride with potassium chloride over a broad range of temperatures and concentrations. Ultrasound speed measurements were performed by the pulse-phase method in which a signal passing through the melt being studied is compared in phase with a standard. The resulting picture is observed on the screen of an oscilloscope. If the phases coincide a maximum appears, while at counterphase there is a minimum. If the frequency of oscillations and wave length are known, one can calculate the speed of ultrasound as their product. The measurement error under the experimental conditions used is 0.2%. For all $KCl-UCl_4$ melts and individual salts studied the speed of ultrasound decreases linearly with increasing temperature, following the equation $C=C_0-aT$. Values of the constants C_0 and a are presented in tabular form. Figure 1; references 8: 5 Russian, 3 Western.
[37-6508]

UDC 546.181:681

VAPOR PHASE SYNTHESIS OF GALLIUM PHOSPHIDE

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHMICHESKAYA TEKHNOLOGIYA in Russian Vol 26, No 8, Aug 83 (manuscript received 26 Feb 83)
pp 899-902

LOBANOV, A. A. and SEVERTSEV, V. N., Chair of Material Sciences, Moscow Institute of Electronic Technology

[Abstract] A mathematical analysis is presented of vapor phase synthesis of gallium phosphide, using a quartz reactor with two heating zones. The input zone was 500 mm long and maintained at 950-1200°C, and GaP precipitation zone was 1000 mm long and maintained at 650-950°C. A mathematical formula was

derived for determining most efficient GaP synthesis for the equipment under consideration, taking into consideration temperature, rate of Ga transfer, and composition of the gaseous phase. At the temperature interval 700-800°C productivity increases with increase in temperature, reaches a maximum, and then decreases sharply, depending on the Cl:H ratio of the starting reagents and the rate of gas flow. Figures 4; references 2: 1 Russian, 1 Western.
[31-12172]

ION EXCHANGE PHENOMENA

UDC 661.183.123.2(088.8)

SYNTHESIS AND STUDY OF CATION EXCHANGE RESIN BASED ON FURFUROL

Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 56, No 9, Sep 83
(manuscript received 17 Mar 81) pp 2082-2085

KHAKIMOV, R. S., FATKHULLAYEV, E. and DZHALILOV, A. T., Tashkent
Polytechnic Institute

[Abstract] Freshly prepared furfurol was placed in a reaction flask with a stirrer, reflux cooler and thermometer and sulfuric acid was introduced as a catalyst at 1:0.05 mass parts with agitation. The reaction mixture was heated in a water bath and condensation performed at 353°K. The reflux cooler was then replaced by a condenser and at 378°K the volatile products of condensation were distilled off until a gel-like mass was produced. The polymer produced was cured at 398-403°K for 10 to 12 hours and ground to a particle diameter of 1.0-1.2 mm. The yield of resin was 88% of the mass of furfurol introduced. The resin produced was sulfurated with concentrated sulfuric acid at a mass ratio of 1:4 mass parts at 413°K for 6 hours or phosphorylated with phosphorus trichloride in the presence of anhydrous AlCl_3 as a catalyst.

IR spectra of the polymers synthesized were produced. The cationites were found to have satisfactory sorption properties for bivalent metals and good chemical and thermal stability. The curves of potentiometric titration of the cationites have the form characteristic for polyfunctional ionites. A change in medium pH has a strong influence on the ion exchange capacity of the ionites synthesized. As pH increases the static exchange capacity for metal ions increases greatly. Homopolycondensation of furfurol with subsequent sulfuration or phosphorylation of the polymers produced thus synthesizes polyfunctional, thermally-stable cation exchange resins with good kinetic and physical-chemical properties. Figures 5; references 12: 11 Russian, 1 Western.
[37-6508]

SYNTHESIS AND STUDY OF CATION EXCHANGE RESINS BASED ON FURFURYL ALCOHOL

Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 56, No 9, Sep 83
(manuscript received 19 Mar 82) pp 2086-2089

KHAKIMOV, R. S., FATKHULLAYEV, E. and DZHALILOV, A. T., Tashkent
Polytechnic Institute imeni A. R. Beruni

[Abstract] Cation exchange resins were synthesized on the basis of furfuryl alcohol and their major properties studied. One mole of freshly prepared furfuryl alcohol was added to a reaction flask equipped with a stirrer, reflux cooler and thermometer and, with agitation, 4 ml of 5% H_2SO_4 were added as a catalyst. The reaction mixture was heated in a water bath and condensation conducted for two hours, decreasing the temperature of the reaction medium to 353°K. The reflux cooler was then replaced by a condenser and volatile products of condensation distilled off at a residual pressure of 70-80 mmHg, 352-356°K, increasing the temperature at the end of the distillation to 373°K. The gel-like mass formed was poured out into a porcelain dish, cured at 413-423°K for 8 hours and ground to a particle size of 1.0-1.2 mm. The yield of the resin was 90% of the mass of the furfuryl alcohol. The resin after preliminary swelling in sulfuric acid was sulfurated at a mass ratio of polymer: H_2SO_4 of 1:6, temperature 413°K, 6 hours. After the reaction was completed the medium was cooled, excess acid removed and the sulfurated mass washed with distilled water until neutral. The synthesized polymer was also synthesized with phosphorus trichloride in the presence of $AlCl_3$ as a catalyst in a flask with a stirrer and reflux cooler at a polymer: $PCl_2:AlCl_3$ ratio of 1:3:0.1 mass parts at 373°K for 6 hours. The polymer was then separated from excess PCl_3 and hydrolyzed with distilled water and ice. As was expected, the thermal stability and chemical stability for corrosive media of the cationites obtained were high, since the ionite consists only of furane rings and active ionogenic groups. The cationites have good sorption properties for alkali earth and polyvalent metals from their solutions. Polycondensation of furfuryl alcohol in an acid medium with subsequent chemical transformation of the polymers produced was thus used to synthesize thermally and chemically stable sulfocationites and phosphoric acid cationites having good sorption and physical-chemical properties. Figures 4; references 8: 6 Russian, 2 Western.

[37-6508]

NITROGEN COMPOUNDS

UDC 547.541.49

PHOTOTROPY OF QUATERNARY AMMONIUM SALTS OF N,N'-BIS-SUBSTITUTED DIIMIDES OF
1,4,5,8-NAPHTHALENETETRACARBOXYLIC ACID CONTAINING BENZENESULFONATE ANIONS

Leningrad ZHURNAL ORGANICHESKOY KHIMII in Russian Vol 19, No 9, Sep 83
(manuscript received 4 Oct 82) pp 1933-1946

KHEYFETS, G. M., Institute of Experimental Medicine, USSR Academy of Medical Sciences, Leningrad

[Abstract] A report is presented on photoreduction of a diimide (Ia), a neuromuscular myorelaxant, and certain other N,N'-substituted 1,4,5,8-naphthalenetetracarboxylic acid diimides which are also interesting from the pharmacologic standpoint. Aqueous solutions of (Ia) sealed in glass ampules are rapidly colored reddish-brown when exposed to natural light, then the color disappears when exposure is stopped. Upon longer exposure the color becomes more intensive and does not disappear, and a brown precipitate forms. Analysis showed that after apparent completion of the process, the solution above the sediment contained 5 to 10% of the initial substance (Ia). This phenomenon, observed in sealed glass ampules, was not observed upon exposure of the same solutions in an open vessel or in ampules containing certain oxidizers such as benzoquinone. The phenomenon of phototropy of aqueous solutions of (Ia) diimide represents photoreduction of the bis cation, severely inhibited by the oxygen of the air. Photolysis of aqueous solutions of (Ia) and (IIa) dibenzenesulfonates involves reduction of only the anions of the salts. Spectroscopic data are presented. Figures 6; references 35: 18 Russian, 17 Western.

[34-6508]

ORGANOMETALLIC COMPOUNDS

UDC 546.23+546.24+517.542.91

RESEARCH IN AREA OF SYNTHESIS OF POLYHALOID ORGANOSELENIUM AND
ORGANOTELLURIUM COMPOUNDS

Baku DOKLADY AKADEMII NAUK AZERBAYDZHANSKOY SSR in Russian Vol 39, No 4,
Jul-Aug 83 (manuscript received 7 May 81) pp 42-45

MAMEDOV, E. Sh., KURBANOV, S. B. and MISHIYEV, R. D., Institute of Chemical
Technology, AzSSR Academy of Sciences

[Abstract] A study of the sequence of addition of selenium halogenides and tellurium halogenides to allyl haloids, especially allylchloride and allylbromide, showed that bis-adducts of the aliphatic series are formed. At room temperatures, and in an ether medium the addition leads to formation of bis-adducts with isomeric structures corresponding to the reaction course, in accordance with, and also contrary to, Markovnikov's rule. References 5: 3 Russian, 1 Western.

[23-2791]

UDC 547.258.11

REACTIVITY OF ORGANIC COMPOUNDS OF TIN, PART 26: REACTION OF (CARBOETHOXYMETHYL)TRIETHYL TIN WITH ALDEHYDES, CATALYZED BY HALIDE IONS, AS A METHOD OF PRODUCING 3-ACETOXYCARBOXYLIC ACID ESTERS

Leningrad ZHURNAL ORGANICHESKOY KHIMII in Russian Vol 19, No 9, Sep 83
(manuscript received 20 Sep 82) pp 1817-1822

BELETSKAYA, I. P., KASHIN, A. N., TUL'CHINSKIY, M. L. and REUTOV, O. A.,
Moscow State University imeni M. V. Lomonosov

[Abstract] The reactions of attachment of (carboethoxymethyl)triethyl tin at the carbonyl group of benzaldehyde, cinnamaldehyde and furfural in the presence of catalytic quantities of tetramethylammonium fluoride were studied. The reactions led to the formation of triethylstannyl alcoholates of the ethyl ester of 3-hydroxycarboxylic acid. The reactions were conducted in DMSO at room temperature, the degree of conversion monitored by PMR. In all cases the reactions occurred as 1,2-attachment, conversion 75-85% in 45-50 hours, with no change upon further continuation of the reaction. The adducts were easily and quantitatively hydrolyzed to form esters of 3-hydroxycarboxylic acids, and were also responsive to acetolysis producing esters of 3-acetoxy-carboxylic acids. Possible reaction mechanisms are discussed and illustrated.

The second catalysis mechanism by halide ions differs in principle from the first with participation of tributyl tin iodide, although in most cases the formation of a common intermediate is assumed--the enol form of (carboethoxy-methyl) triethyl tin. References 22: 9 Russian, 13 Western.
[34-6508]

ORGANOPHOSPHORUS COMPOUNDS

UDC 547.25'118

REACTION OF TETRAALKYL PYROPHOSPHITES AND DIETHYLACYLPHOSPHITE WITH TRIFLUOROACETIC ACID: TRIFLUOROACYLPHOSPHITES AND TRIFLUOROKETOPHOSPHONITES

Leningrad ZHURNAL OBSHCHEY KHMII in Russian Vol 53, No 9, Sep 83
(manuscript received 2 Aug 82) pp 1941-1944

OFITSEROV, Ye. N., MIRONOV, V. F., KONOVALOVA, I. V. and PUDOVIK, A. N., Kazan State University imeni V. I. Ul'yanov-Lenin

[Abstract] A previous report studied the reactions of α -phosphorylated trialkylphosphites with CF_3COOH under various conditions. Continuing these studies, the authors discuss the interaction of tetraalkylpyrophosphites $(\text{RO})_2\text{POP(OR)}_2$, where R=Pr (I), Et (II) and acylphosphite $(\text{EtO})_2\text{POC(O)CH}_3$ (III), with CF_3COOH in CH_3CN with ratios of the reagents 1:1 and 1:2 for the compounds (I, II). Compound (I) was reacted with CF_3COOH at -30 to -50°C, (II) at +5 to +15°C. The relationship and composition of products remained constant within these temperature intervals. PMR, ^{19}F and ^{31}P NMR and IR spectra were recorded. It was found that the interaction of tetraalkylpyrophosphites and diethylacylphosphite with CF_3COOH forms α -phosphonoalkylphosphates, as a result of multistage transformation of the initially-generated trifluoroacylphosphite and trifluoroketophosphonates, plus complexes of dialkylphosphites with trifluoroacetic acid. References 7 (Russian).

[39-6508]

UDC 547.26'118

REACTIONS OF PYROCATECHIN TRIFLUOROACYLPHOSPHITE WITH ALCOHOLS AND ACIDS

Leningrad ZHURNAL OBSHCHEY KHMII in Russian Vol 53, No 9, Sep 83
(manuscript received 2 Aug 82) pp 1945-1950

KONOVALOVA, I. V., OFITSEROV, Ye. N., MIRONOV, V. F., KOSTYUK, V. I. and PUDOVIK, A. N., Kazan State University imeni V. I. Ul'yanov-Lenin

[Abstract] Data are presented on reactions of pyrocatechin trifluoroacetylphosphite (I) with aliphatic, fluorinated, α -functionally substituted alcohols, trifluoroacetic, trichloroacetic and hydrochloric acids. Acylphosphite (I) was selected because of its stability to Arbuzov isomerization at elevated

temperatures. Phosphite (I) is also resistant to the effects of equimolar quantities of CF_3COOH both at room temperature and at 50°C and higher. This is explained by the displacement of the equilibrium of the reversible reaction of (I) in the direction of the initial products, the stability of the acyl-phosphite to isomerization to ketophosphonate and the absence of attachment of the ketophosphonate to the acylphosphite. This explanation was tested experimentally. The reaction which occurs between (I) and the acids mentioned, tetrafluoropropanol, α -oxyphosphonate and cyclic phosphorous acids is not the Arbuzov reaction, but rather replacement of a trifluoroacyl group with the corresponding acid or alcohol radical with preservation of the valence of the phosphorus atom. References 11 (Russian).

[39-6508]

UDC 542.91+547.1'118

INTERACTION OF 4,5-BENZO-1,3,2-DIHETEROPHOSPHOLANES WITH AMINES

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 53, No 9, Sep 83
(manuscript received 19 Nov 82) pp 1950-1954

PUDOVIK, M. A., MIKHAYLOV, Yu. B. and PUDOVIK, A. N., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] The authors recently demonstrated the possibility of aminolysis of the endocyclic P-N bond in 5-membered heterocycles. Continuing this work, a study was made of the reaction of 4,5-benzo-1,3,2-thiaza- and -dioxaphospholanes with primary and secondary amines. Aminolysis of 2-ethyl-4,5-benzo-1,3,2-thiazaphospholane (I) and 2-ethyl-3-methyl-4,5-benzo-1,3,2-thiazaphospholane (II) does not occur at room temperature or upon heating to 100°C for two hours. However, 2,3-substituted-1,3,2-oxazaphospholanes react exothermically with aniline hydrochloride forming the amidophosphite (III) with quantitative yield in a reversible reaction, the motive force of which is the formation of more stable amine salts. The reaction of 2-ethyl-4,5-benzo-1,3,2-dioxaphospholane (VI) with various amines revealed that as the basicity of the secondary amines decreases their reactivity for dioxaphospholanes (VI) decreases. Various characteristics of the reaction indicate that the first stage in aminolysis includes nucleophilic attack of the amine on the trivalent phosphorus atom. It was found that the reactivity of secondary amines for 2-ethyl-4,5-benzo-1,3,2-dioxaphospholanes increases with increasing basicity. The interaction of 2-ethyl-4,5-benzo-1,3,2-dioxaphospholane with benzyl- and sec.-butylamines yields products of attachment, monocyclic phosphoranes with the P-H bond, which were determined spectrally. References 10: 5 Russian, 5 Western.

[39-6508]

UDC 547.26'118

INTERACTION OF PHOSPHORUS ACID ESTERS WITH TRIVALENT PHOSPHORUS CHLORIDES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 9, Sep 83
(manuscript received 30 Nov 82) pp 1954-1957

GAZIZOV, T. Kh., BELYALOV, R. U. and PUDOVIK, A. N., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] The interaction of trialkylphosphites with PCl_3 and alkylidichlorophosphites is an exchange of the alkoxy group of trialkylphosphite for a chlorine atom of the corresponding P (III) chloride. To determine the mechanism of this reaction, the authors used ^{31}P NMR to study the reaction of various phosphorus acid esters with P (III) chlorides. As a result it was found that as the size and electron acceptor capacity of the phosphite radicals increase, there is a significant slowing of the reaction rate. The data obtained in general show that the reaction of phosphorus acid esters with P (III) chloride is most satisfactorily explained by a reaction system in which the first stage is reaction of the derivatives of P (III) acids with P (III) halides to form products having the P-P bond. It is possible that the intermediate product containing the P-P bond decomposes further to complete ionization of the quasiphosphonium compound. In reactions of asymmetrical P (III) acid esters with P (III) chlorides, the RO group at the chlorine atom containing the more electron accepting radical is preferentially substituted. Analysis of the data produced as well as data from the literature indicate that the P (III) acid ester RO group exchange reaction at the chloride chlorine atom begins with nucleophilic interaction of the phosphorus atom of phosphite with the phosphorus atom of the P (III) chloride and continues through intermediate products containing the P-P bond. References 10: 7 Russian, 3 Western.

[39-6508]

UDC 547.341

REACTIVITY OF IODINE AND INTERHALIDES WITH SUBSTITUTED ALLENEPHOSPHONIC ACID ESTERS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 9, Sep 83
(manuscript received 12 Aug 82) pp 1958-1960

ANGELOV, Kh. M., YENCHEV, D. D. and KIRILOV, M., Higher Pedagogic Institute, Shumen; Sofia University, Sofia

[Abstract] It has been established in recent years that the main reaction path in chlorination and bromination of substituted allenephosphonic acid derivatives is the formation of 1,2-oxaphosphol-3-ene derivatives. Continuing these studies, in this work the authors studied the reactions of iodine,

chloroiodine and bromoiodine with 3,3-disubstituted allenephosphonic acid esters. It was established that in all cases iodine derivatives of 1,2-oxaphosphol-3-ene were produced. 4-iodo-2-oxo-1,2-oxaphosphol-3-enes were isolated after distillation of the solvent by recrystallization from heptane or hexene. These are colorless crystals produced in low yield due to resinification during the reaction. The composition and structure of the compounds produced were confirmed by spectral studies and elemental analysis. The relative reaction rate of the interaction of halides with 3-methyl-1,2-butadiene phosphonic acid dimethyl ester was studied at 20°C. The reaction was fastest with iodine chloride, then bromide, then finally iodide. The experimental results indicate an ionic interaction of halides with substituted allenephosphonic acid esters. References 7 (Russian).
[39-6508]

UDC 547.26'118+547.494

OPTICALLY ACTIVE α -PHOSPHORYLATED BENZYLISOCYANATES

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 53, No 9, Sep 83
(manuscript received 28 Jul 82) pp 1960-1967

KOZHUSHKO, B. N., LOMAKINA, A. V., PALIYCHUK, Yu. A. and SHOKOL, V. A., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] To synthesize optically active α -(diethoxyphosphonyl)benzylisocyanate a method suggested earlier was used, based on the use of levorotary α -(diethoxyphosphonyl)benzylamine as the initial compound. When phosgene acts on (S)(-)- α -(diethoxyphosphonyl)benzylamine in the presence of pyridine, (S)(+)- α -(diethoxyphosphonyl)benzylisocyanate is produced with good yield which, when treated with one mole of phosphorus pentachloride is converted to (S)(+)- α -(ethoxychlorophosphonyl)benzylisocyanate. When this compound is interacted with arsenic trifluoride, (S)(+)- α -(ethoxyfluorophosphonyl)benzylisocyanate is formed. When (S)(+)- α -(diethoxyphosphonyl)benzylisocyanate is interacted with ethyl alcohol and p-chloroaniline, optically active ethyl ester and p-fluorophenylamide of (S)(-)-N-[α -(diethoxyphosphonyl)benzyl]carbaminic acid are produced. When the isocyanate is heated in toluene in the presence of catalytic quantities of 1,3-dimethylphosphol-3-ene, optically active (SS)(-)-N, N'-bis[α -(diethoxyphosphonyl)benzyl]carbodiimide is produced. (S)(+)- α -(diethoxyphosphonyl)benzylisocyanate easily reacts with (S)(-)- α -(diethoxyphosphonyl)benzylamine, forming (SS)(-)-N,N'-bis[α -(diethoxyphosphonyl)benzyl]-urea. The optically active α -(diethoxyphosphonyl)-, α -(ethoxyhalogenphosphonyl)- and α -dihalogenphosphonyl)benzyl isocyanates are colorless liquids easily hydrolyzed by moist air, which can be distilled under a vacuum without decomposition. Derivatives of α -phosphorylated benzylisocyanates are colorless crystalline substances. The structure of the isocyanates and their derivatives were confirmed by IR and NMR spectroscopy. Figure 1; references 15: 10 Russian, 5 Western.
[39-6508]

UDC 541.6:547.1.118

PHOTOELECTRON SPECTRA AND ELECTRON STRUCTURE OF ORGANOPHOSPHORUS COMPOUND:
COMPOUNDS OF COORDINATED PHOSPHORUS WITH PHOSPHORUS-SULFUR BOND

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 53, No 9, Sep 83
(manuscript received 26 Nov 82) pp 1968-1974

ZVEREV, V. V., BAZHANOVA, Z. G., VILLEМ, N. V. and VILLEМ, Ya. Ya., Institute
of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR
Academy of Sciences; Tartu State University

[Abstract] Continuing study of photoelectron spectra and electron structure
of the molecules of organic compounds of phosphorus, the authors studied the
spectra of a number of these compounds with the phosphorus-sulfur bond. The
spectra were studied and vertical ionization potentials determined of diethyl-
ethylthiophosphinite (II), methyldichlorothiophosphite (III), methyldimethyl-
dithiophosphonite (IV), trimethyltrithiophosphite (V), triethyltrithio-
phosphate (VI) and ethyldichlorophosphine (VII). The electron structure of
thiophosphinite (I) and thiophosphonite (IV) were calculated with variation of
the angles of rotation around the P-S bond. The spectra were recorded on a
photoelectronic spectrometer with a helium resonant radiation source. It was
found that as the number of thio groups increases, the first ionization
potential of the molecule decreases, but the energy of the orbital of the
unshared pair of phosphorus increases. A change in direction of protonation
and alkylation of molecules in the series $P(SMe)_n Me^{3-n}$ results from the
relationship of nS and nP orbitals in these molecules, Figures 2;
references 20: 16 Russian, 4 Western.

[39-6508]

UDC 547.241

INTERACTION OF PERFLUOROIODOALKANES WITH TRIVALENT PHOSPHORUS ACID ESTERS,
PART 7: STUDY OF KINETICS AND MECHANISM OF REACTION OF 1-IODOHEPTAFLUORO-
PROPANE WITH TRIALKYLPHOSPHITES

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 53, No 9, Sep 83
(manuscript received 4 Nov 82) pp 1974-1978

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[Abstract] A study is made of the reaction of 1-iodoheptafluoropropane with
trialkylphosphites, as a part of the continuing study of the mechanism of the
Arbuzov regrouping reaction. The data on the kinetics of the reaction of
 C_3F_7I with trialkylphosphites agree with the presumption of participation of
intermediate complexes, the existence of which was demonstrated by direct
methods. The experimental data allow a reaction mechanism for iodofluoro-
alkylation of trivalent phosphorus acid esters to be suggested. To refine the
nature of the stage of decomposition of the intermediate complex with charge

transfer into the reaction products, the influence of a number of inhibitors and initiators on the rate of thermal and photochemical reactions of iodofluoroalkylation of trialkylphosphites and phosphonites was studied. A comparison of the results and kinetic data rather convincingly indicates that the reaction mechanism suggested is accurate. The first stage of the Arbuzov regrouping in a number of perfluoroiodoalkanes is thus demonstrated to be formation of complexes with charge transfer of moderate energy. These complexes are then further converted to the end products. Figures 3; references 13: 9 Russian, 4 Western.

[39-6508]

UDC 547.241

INTERACTION OF PHOSPHORUS ACID ESTERS WITH PERFLUORINATED CARBOXYLIC ACID ANHYDRIDES: CALORIMETRY, IR SPECTRA

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 53, No 9, Sep 83
(manuscript received 6 Dec 82) pp 1979-1982

ALEYNIKOV, S. F., KRUTIKOV, V. I., LAVRENT'YEV, A. N., BAKHMUTOV, Yu. L.
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[Abstract] A study was made of the interaction of phosphorus acid esters with anhydrides of perfluorocarboxylic acids $(RO_2)_2\text{PHO} + (\text{R}'\text{CO})_2\text{O}$ ($\text{R}=\text{CH}_3, \text{C}_2\text{H}_5,$ iso- $\text{C}_3\text{H}_7, \text{HCF}_2\text{CF}_2\text{CF}_2$; $\text{R}'=\text{CH}_3, \text{CF}_3, \text{C}_2\text{F}_5, \text{C}_3\text{F}_7, \text{HCF}_2\text{CF}_2$) by calorimetric titration. Analysis of the variation in change of temperature in the calorimeter measurement cell as a function of the ratio of number of moles of acceptor and donor shows that initially in this system a molecular complex with a composition of 1:2 is formed, followed by a composition of 1:1. The experimental data indicate that in the concentration interval of 0.11 to 0.025 mol/l the equilibrium constant does not vary with concentration, indicating its correctness for the entire reaction series $(RO_2)_2\text{PHO} + (\text{R}'\text{CO})_2\text{O}$. Analysis of thermodynamic parameters of both complexes indicates that the 1:2 complex is initially stronger than the 1:1 complex. As the polarity of the solvent used increases, the complex formation content decreases and enthalpy increases. This is probably not a result of the influence of polarity of the solvent, but rather presence of specific solvent properties, such as the capability of chloroform to form H bonds. Figures 2; references 7 (Russian).

[39-6508]

UDC 547.241

INTERACTION OF P (III) ACID ESTERS WITH CARBON TETRACHLORIDE, PART 4:
DEGREE OF CHARGE TRANSFER IN DA-COMPLEXES

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 53, No 9, Sep 83
(manuscript received 6 Dec 82) pp 1982-1985

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[Abstract] Alkyl esters of phosphonous acids form complexes of the composition 1:1 with CCl_4 . The equation $\delta \sim 1.42\delta\eta/\eta + 0.02$, where $\delta\eta/\eta$ is the relative change in frequency of valent oscillations during complex formation is used to calculate the degree of charge transfer in these complexes based on the shift in oscillating frequency of the (P-O)-C bond. The degree of charge transfer thus computed from IR spectral data agrees well with the enthalpy of complex formation. During complex formation the (P-O)-C bond is elongated, changing the degree of occupation of the d-orbital of phosphorus in the P-O bond. Figure 2; references 8: 6 Russian, 2 Western.
[39-6508]

UDC 541.11:547.468

DISSOCIATION OF OXYETHYLIDENEDIPHOSPHONIC ACID IN AQUEOUS SOLUTIONS

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 53, No 9, Sep 83
(manuscript received 28 Dec 82) pp 1985-1989

VASIL'YEV, V. P., ZAYTSEVA, G. A., KOZLOVSKIY, Ye. V. and BORISOVA, I. N.,
Ivanovo Institute of Chemical Technology

[Abstract] Experimental data on the dissociation of oxyethylidenediphosphonic acid in the presence of NaCl were processed by computer using a universal program designed for calculation of equilibrium constants in systems with arbitrary numbers of reactions based on measured equilibrium concentrations of one of the particles. The major subsections of the program used include calculation of equilibrium compositions, search for a minimum of a function, calculation of standard deviations of desired parameters and correlation coefficients, and allow calculation of $\log K$ of all equilibria in the system or of just a few. The effective dissociation constants were calculated with values of ionic force 0.2, 0.5 and 1.0, and it was found that the results of potentiometric titration in the presence of sodium chloride can yield an unambiguous conclusion concerning the dissociation of the acid beyond the 4th power. Figures 1; references 11: 5 Russian, 6 Western.
[39-6508]

UDC 547.26'118

INTERACTION OF POLYFLUORINATED ALIPHATIC ALDEHYDES WITH TRIVALENT PHOSPHORUS COMPOUNDS: 2,2,2-TRIALKOXY-2,2-DIHYDRO-3,5-BISPOLYFLUOROALKYL-1,4,2-DIOXAPHOSPHOLANES

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 53, No 9, Sep 83
(manuscript received 22 Nov 82) pp 1994-2000

MARKOVSKIY, L. N., KOLESNIK, N. P., BAKHMUTOV, Yu. L., KUDRYAVTSEV, A. A., and SHERMOLOVICH, Yu. G., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] A study was made of the reaction of polyfluoro-containing aldehydes with trimethyl- and tris (2,2,3,3-tetrafluoropropyl)phosphites. Trimethylphosphite reacts with 2,2,3,3-tetrafluoropropanal, 2,2,3,3,4,4,5,5-octafluoropentanal and 2,2,3,3,4,4,5,5-octafluoro-5-chloropentanal to form 2,2,2-trimethoxy-2,2-dihydro-3,5-bispolyfluoroalkyl-1,4,2-dioxaphospholanes (III). The reaction occurs at -70 to -80°C and is accompanied by slight polymerization of the aldehyde, which is usually therefore taken in some excess.

The ^{31}P NMR spectra of the reaction products confirm the penta-coordination state of the phosphorus in 1,4,2-dioxaphospholanes (III). Compounds (III) are distilled in a vacuum of 0.1 mmHg in the 100 to 120°C temperature interval, but the distilled products show signals in the NMR spectra indicating presence of dimethylmethanephosphonate and trimethylphosphate, indicating thermal instability of (III). The thermal stability of 1,4,2-dioxaphospholanes (III) increases significantly with increasing number of electron acceptor substituents at the phosphorus atom. The reaction of dialkylphosphites with polyfluoro-aliphatic aldehydes can serve as a method of synthesis of α -hydroxypoly-fluoroalkanephosphonic acid derivatives. References 15: 9 Russian, 6 Western.
[39-6508]

UDC 547.341

SYNTHESIS AND PROPERTIES OF PYROCATECHINPHOSPHONOACETIC ACID ESTERS

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 53, No 9, Sep 83
(manuscript received 7 Jan 83) pp 2000-2003

ISMAGILOV, R. K., RAZUMOV, A. I., ZYKOVA, V. V. and NIYAZOV, N. A., Kazan Institute of Chemical Technology imeni S. M. Kirov

[Abstract] A study of the reaction of ethyl ester of pyrocatechinphosphorous acid with ethyl esters of halogen (chloro-, bromo-, iodo-) acetic acids showed that at high temperatures, Arbuzov regrouping occurs, leading to the formation of ethylpyrocatechinphosphonoacetate (I) with moderate yields. The reaction was studied by differential thermographic analysis. Product (I) is a colorless viscous liquid soluble in organic solvents. The ^{13}C NMR spectrum confirms its phosphonate structure. The same compound was obtained by cross synthesis - oxidation of cyclic pyrocatechin ester of carboethoxymethylphosphonous acid

(II), formed by interaction of ethyltriethylstannyl acetate with pyrocatechin-chlorophosphite in a C-alkylation reaction. Figures 2; references 3: 2 Russian, 1 Western.
[39-6508]

UDC 547.241

REACTION OF PHOSPHOROUS ACID HEXAETHYLTRIAMIDE WITH VICINAL DIBROMIDES AND 1,2,3-TRIBROMOPROPANE. A CONVENIENT METHOD OF DEBROMINATION

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 53, No 9, Sep 83
(manuscript received 24 Dec 82) pp 2003-2008

MIZRAKH, L. I., POLONSKAYA, L. Yu., BABUSHKINA, T. A. and IVANOVA, T. M.

[Abstract] Hexaethyltriamidophosphite was reacted with dibromoethane, producing a crystalline compound (I) unstable in air which, like hexaalkyltriaminophosphonium salts studied earlier, forms a complex with thiocarbamide (II) with good yield. The composition of the complex depends on the quantity of thiocarbamide taken in the reaction. With an initial molar ratio of substance (I) and thiocarbamide of 1:0.7-0.8, a complex with the composition 1:2 (IIa) is formed, while with an initial ratio of 1:3-3.5 the complex has the composition of 1:4 (IIb). Elemental analysis and ^1H , ^{13}C and ^{31}P NMR spectral analysis of compound (IIa, b) indicates that it is a mixture of thiocarbamide with bromo(hexaethyltriamino)phosphonium bromide. The interaction of hexaethyltriamidophosphite with dibromoethane is thus demonstrated to result in the formation of a triaminophosphonium salt containing the PBr bond. Compound (I) is formed both with equimolar ratio of dibromoethane and hexaethyltriamidophosphite and with a ratio of 1:2. Hexaethyltriamidophosphite is found to be a more powerful and universal debrominating agent than thiocarbamide and the reaction which has been discovered can obviously serve as a method of synthesis of olefins from vicinal dibromides. References 5: 4 Russian, 1 Western.
[39-6508]

UDC 542.398

HYDROLYSIS OF THE PYROPHOSPHATE BOND IN OXIDATION-REDUCTION SYSTEMS

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 53, No 9, Sep 83
(manuscript received 29 Dec 82) pp 2008-2012

MURADOV, A. Z. and YASNIKOV, A. A., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] A search was undertaken for chemical reactions in which the decomposition of the pyrophosphate bond is accompanied by oxidation-reduction processes as is the case in many biochemical systems. Acceleration of the

reaction of hydrolysis of the pyrophosphate ion in the presence of manganese dioxide and in the Ag^+ -cysteine system was discovered and studied. The reaction of decomposition of the pyrophosphite ion in the presence of MnO_2 is described by a first order kinetic equation with respect to the pyrophosphate. The influence of MnO_2 appears most strongly at lower pH values. The activation energy for hydrolysis of the pyrophosphate ion in the presence of MnO_2 at 60- 80°C is 22.3 kcal/mol. Introduction of permanganate ions to the reaction system strongly suppresses the catalytic effect of MnO_2 . Other oxidizers have no influence on the catalytic effect of MnO_2 , indicating the specific effect of the permanganate ion. Decomposition of the pyrophosphate bond is accompanied by an oxidation-reduction reactions of MnO_2 leading to the formation of Mn^{2+} and MnO^{4-} ions at high concentrations of pyrophosphate, whereas at pyrophosphate concentration not over $3 \cdot 10^{-3}$ mol/l, MnO_2 is not converted during the course of the reaction. In the Ag^+ -cysteine system, reduction of the Ag^+ ion by cysteine is accompanied by decomposition of the pyrophosphate bond in pyrophosphate, tripolyphosphate and ATP. These reactions can be used as models in the interpretation of the mechanism of participation of ATP in many biochemical processes. References 12: 7 Russian, 5 Western.
[39-6508]

UDC 547.26'118

PHOSPHORUS-CONTAINING CROWNS, PART 5: EXTRACTION AND SPECTRAL PROPERTIES OF POLYMORPHOUS MODIFICATIONS OF DIBENZOTRIPHENYLPHOSPHAZOPHONYL-14-CROWN-5

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 53, No 9, Sep 83
(manuscript received 11 Jan 83) pp 2012-2015

PINCHUK, A. M., ZASORINA, V. A., SHTEPANEK, A. S., ROZHKOVA, Z. Z., SOLOTNOV, A. F. and RAYEVSKIY, O. A., Institute of Physiologically Active Substances, USSR Academy of Sciences, Chernogolovka; Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Results are presented from continued detailed study of the interaction of triphenylphosphazodichlorophosphonyl with the disodium derivative of bis[2-(o-oxyphenoxy)-ethyl]ether using various solvents, temperature conditions and methods of treatment of the specimens. Variation of external conditions leads to production not only of dibenzotriphenylphosphazophonyl-14-crown-5 (I) described earlier but other compounds as well with identical molecular weight and elemental analysis data but with different melting points. IR and NMR spectra are used to determine the structure of the products produced. Although the spectra are identical under many conditions in various solvents, the IR spectra in the solid phase differ significantly. The major differences in the spectra of the solid specimens are related to oscillations of methylene groups. Apparently, different interactions of these groups in different molecules are observed for the two higher melting point modifications of the substance. Figure 1; references 7: 6 Russian, 1 Western.
[39-6508]

UDC 547.341.07

STUDY OF REACTIONS OF ADDUCTS OF PHOSPHORUS PENTACHLORIDE AND STYRENE WITH ARSENIC TRIFLUORIDE

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 53, No 9, Sep 83
(manuscript received 4 Jan 83) pp 2020-2024

FRIDLAND, S. V., DMITRIYEVA, N. V. and MIFTAKHOV, M. N.

[Abstract] A study is made to determine the influence of the nature of substituents in benzene derivatives on the yield of a product of attachment and the conditions of formation of the product of arylation. For this purpose reactions were performed in toluene, ethylbenzene, isopropylbenzene and chlorobenzene. Reaction conditions were identical: ratio of styrene to phosphorus pentachloride 1:1.5, adduct produced at 2-5°C. After the adduct was held at 15-20°C for 5 hours it was treated with a calculated quantity of arsenous trifluoride at 0-5°C. In all cases products of attachment of the fragment of the solvent at the multiple bond were produced; when chlorobenzene was used as the solvent, β -styryl tetrafluorophosphorane was also produced. The presence of arsenous trifluoride and phosphorus pentachloride or their adducts was found to have a catalytic effect on the formation of the product of attachment. It was found that an electronegative substituent decreases the yield of the product of attachment at the double bond. References 5: 4 Russian, 1 Western.
[39-6508]

UDC 543.422.25

^{77}Se and ^{31}P NMR SPECTRA OF ORGANOSELENOPHOSPHORUS COMPOUNDS

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 53, No 9, Sep 83
(manuscript received 10 Jan 83) pp 2143-2144

YENIKEYEV, K. M., BAYANDINA, Ye. V., ISMAYEV, I. E., BUINA, N. A., IL'YASOV, A. V. and NURETDINOV, I. A., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] Parameters of the ^{77}Se and ^{31}P NMR spectra of a number of organoselenophosphorus compounds are presented. The spectra were produced on a West German Bruker type WM-250 spectrometer at 47.699 and 101.27 MHz for ^{77}Se and ^{31}P , respectively. The values of δ_{Se} of the compounds were found to vary over broad limits. Displacement of the signals upon transition from $(\text{C}_6\text{H}_5)_3\text{PSe}_2(\text{C}_6\text{H}_5)\text{PSeCl}_2$ is explained by the decrease in contribution of the bipolar $\text{P}^+-\text{Se}-$ structure to the shielding of the selenium nucleus.
References 2 (Western).
[39-6508]

UDC 547.783

SYNTHESIS OF PHOSPHORYLATED HYDANTOINS

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 53, No 9, Sep 83
(manuscript received 28 Feb 83) pp 2146-2147

KHOKHLOV, P. S., KASHEMIROV, B. A., MIKITYUK, A. D. and STREPIKHEYEV, Yu. A.,
Moscow Institute of Chemical Technology imeni D. I. Mendeleyev,
All-Union Scientific Research Institute of Phytopathology, Golitsyno,
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[Abstract] The authors report their synthesis, from esters of oximino phosphonoacetic acid, of the first representatives of the phosphorylated hydantoins: triethyl ester of 1-N-methyl-4-phosphonohydantoic acid; triethyl ester of 1-N-phenyl-4-phosphonohydantoic acid; 3-methyl-5-diethoxyphosphorylhydantoin; 3-phenyl-5-diethoxyphosphorylhydantoin are synthesized and PMR spectra produced. Details of synthesis are given.

[39-6508]

UDC 547.538:542.945.3

REACTION OF CYCLOHEXENE WITH ORGANYLCHLOROPHOSPHONIUM HEXAFLUOROPHOSPHATES

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 53, No 9, Sep 83
(manuscript received 23 Feb 83) pp 2149-2150

DMITRIYEV, V. K. and TIMOKHIN, B. V., Irkutsk State University imeni
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[Abstract] It was found that cyclohexene (I) interacts with chlorophosphonium derivatives of $R\text{PCl}_n^{+}4-n\text{PCl}_6^{-}$, forming the corresponding chlorophosphane, phosphorus trichloride and products of chlorination of the alkene-trans-dichlorocyclohexane (II) and 3-chlorocyclohexene (III). This indicates that the reaction of the symmetrical alkene with chlorophosphonium derivatives is a halogenophilic reaction, the major event of which is alkene attack of the chlorine atom in the phosphonium cation. Equivalent quantities of the reagent were reacted in a sealed ampule in an atmosphere of dry argon at controlled temperature. The yield of chlorination products was determined by GLC, and ^{31}P NMR spectra were produced.

[39-6508]

UDC 547.298.5

PHOSPHOROTROPIC TAUTOMERISM IN SERIES OF PHOSPHORYLATED AND THIOPHOSPHORYLATED 2-ETHYLAMINODIHYDRO-1,3-TIAZINES

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 271, No 3, Jul 83
(manuscript received 30 Mar 83) pp 633-636

BOGEL'FER, L. Ya., GONCHAROVA, Ye., L., GRAPOV, A. F., NEGREBETSKIY, V. V., RAZVODOVSKAYA, L. V., ENGLIN, V. M. and N. N. MEL'NIKOV, corresponding member, USSR Academy of Sciences, All-Union Scientific Research Institute of Chemical Agents for Plant Protection, Moscow

[Abstract] Processes of phosphorotropic tautomerism in phosphoryl- and thiophosphoryl-derivatives of 2-ethylamino-dihydro-1,3-thiazines (I-IV) were studied by nuclear magnetic resonance methods. Compounds (I-IV) were obtained by interaction of 2-ethylamino-dihydro-1,3-thiazine with chloranhydrides of oxygen and thioacids of phosphorus in anhydrous benzene at 50 to 70 degrees centigrade for several hours. The ratio of tautomeric forms (imino and amino) in solutions of compounds (I-IV) depended on the nature of the substituents on the phosphorous atom, the polarity of the medium and the temperature. The level of form (B) increased above substitution of the methyl group in the phosphorous atom by a phenoxy group, during transition from phosphoryl- to methyl-derivatives and also with an increase of polarity of the medium. The level of tautomeric forms depended little on the temperature for thiophosphoryl compounds II and IV while the level of form A increased with the temperature increase. Calculated and found values are compared and discussed. References:

6 Russian.

[12-2791]

UDC 541.6:542.91:547.427.3:546.183.2'131

REACTION OF MANNITOL WITH PCl_3 AND PRODUCT STRUCTURE

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHMICHESKAYA in Russian No 9, Sep 83 (manuscript received 22 Nov 82) pp 2068-2074

LITVINOV, I. A., CHEREPINSKIY-MALOV, V. D., STRUCHKOV, Yu. T., ARBUZOV, B. A., GURARIY, L. I., PLYAMOVATYY, A. Kh. and MUKMENEV, E. T., Institute of Heteroorganic Chemistry imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow; Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] The structures of the products obtained by the reaction of mannitol with PCl_3 in anhydrous dioxane at 55-60°C, 1,2,4;3,5,6-bis-O-(phosphite)mannitol³ (I) and 1,2;3,4;5,6-tris-O-(chlorophosphite)-mannitol (II), were investigated by means of x-ray structural analysis and the method of molecular mechanics. Evaluation of I shows that two 2,7,8-trioxa-1-phosphabicyclo [3.2.1] octane fragments are joined in such a manner that the incorporated six-membered

rings form a 2,4,7,9-tetraoxa-3,8-diphosphabicyclo[4.4.0]decane system with the internal-o conformation. Studies on II showed that the most stable diastereomers possess a central ring with the chair conformation, while the external rings have identical conformations of the envelope-type. Figures 3; references 9: 6 Russian, 3 Western.
[28-12172]

UDC 543.422.25:542.91:547.1'118

REACTIONS OF ALKYLTHIOCHLOROPHOSPHONITES AND DIALKYLCHLORODITHIOPHOSPHITES WITH CARBONYL COMPOUNDS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHMICHESKAYA in Russian No 9, Sep 83 (manuscript received 15 Dec 82) pp 2114-2121

KARDANOV, N. A., PROVOTOROVA, N. P., PETROVSKIY, P. V., GODOVIKOV, N. N., and KABACHNIK, M. I., Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow

[Abstract] Reaction mechanisms are presented for the synthesis of thiol esters of alpha-hydroxyalkylthiophosphonic acids which may be of physiological interest via addition reactions between S-alkyl thiophosphonites and carbonyl compounds. The specific reactions covered are those between S-alkylchlorothiophosphonites and S,S-dialkylchlorodithiophosphites with various aldehydes and ketones in the presence of OH-compounds. S-alkylthiophosphonites were found to be unstable and unobtainable in the free state. They are highly reactive at the instant of formation and enter into addition reactions with aldehydes and ketones. Sulfur-free phenyl phosphonites were obtained by the reaction of PhP(Cl)SEt with aliphatic alcohols and carboxylic acids. References 15: 10 Russian, 5 Western.

[28-12172]

UDC 547.241

B-PHOSPHORYLATED ENAMINES

Leningrad ZHURNAL OBRASHCHEY KHMII in Russian Vol 53, No 8, Aug 83 (manuscript received 21 Feb 83) pp 1689-1693

MEL'NIKOV, N. N., KOZLOV, V. A., CHURUSOVA, S. G., BUVASHKINA, N. I., IVANCHENKO, V. I., NEGREBETSKIY, V. V. and GRAPOV, A. F., All-Union Scientific Research Institute of Chemical Means of Plant Protection, Moscow

[Abstract] Synthesis of β -phosphorylated enamines was achieved by the condensation of compounds containing a mobile hydrogen atom with amide acetals. The general approach consisted of reacting equimolar concentrations of a phosphorus-containing CH acid (using compounds with different acidities of the CH fragment) with dimethylacetal dimethylformamide (I) at 100°C under argon and analysis of the products by silica gel TLC to follow the course of the reaction. The

activated methylene phosphonates reacted with I exothermally with the yields of the phosphorylated enamines proportional to CH acidity. Condensation of I with cyanomethylene phosphonate and phosphoacetone, in which the nitrile and acyl groups were replaced by carbalkoxy and carbamoyl groups on the methylene phosphonate to reduce CH acidity, required prolonged heating for reaction to occur. The significance of steric factors was illustrated by O,O-diethyl-carbotertbutoxymethylene phosphonate in which the bulky tert-butyl radical interfered with the reactive site and accounted for the low reactivity of the molecule. IR and ESR spectra provided data indicating rotation around the C=C and C-N bonds in the β -phosphorylated enamines. References 11: 6 Russian, 5 Western.

[24-12172]

UDC 547.241

PHOSPHORYLATION AND THIOPHOSPHORYLATION OF AMINOTHIADIAZOLES,
AMINOXADIAZOLES AND AMINOXAZOLINES

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 53, No 8, Aug 83
(manuscript received 21 Feb 83) pp 1693-1700

MEL'NIKOV, N. N., RAZVODOVSKAYA, L. V., VOROB'YEVA, N. N., LI, V.D.,
KARASEVA, T. A., GOLOVKIN, G. V., BOGEL'FER, L. Ya., NEGREBETSKIY, V. V. and
GRAPOV, A. F., All-Union Scientific Research Institute of Chemical Means of
Plant Protection, Moscow

[Abstract] To expand available knowledge on the phosphorylation and thiophosphorylation of aminoheterocycles, studies were conducted on the phosphorylation and thiophosphorylation of 2-amino-1,3,4-thiadiazole, 2-amino-1,3,4-oxadiazole, and 2-aminoxazoline with phosphorus (IV) oxyacid chlorides. Reactions involving 5-substituted 2-amino-1,3,4-thiadiazoles in anhydrous solvents led to products in which either exocyclic nitrogen was thiophosphorylated or the two nitrogen atoms within the heteroring were thiophosphorylated, depending on the nature of the substituent. Thiophosphorylation of 5-methyl(phenyl)-2-amino-1,3,4-oxadiazoles involved the exocyclic nitrogen, while in the case of 2-aminoxazoline the two ring nitrogens were simultaneously thiophosphorylated. Phosphorylation of 2-amino-1,3,4-thiadiazoles involved only the exocyclic nitrogen; the products of 2-amino-1,3,4-oxadiazole and 2-aminoxazoline phosphorylation were highly susceptible to hydrolysis.

References 9: 5 Russian, 4 Western.

[24-12172]

UDC 547.241

PHOSPHORYLATED AND THIOPHOSPHORYLATED 3-AMINO-1,4-BENZOTIAZINE DERIVATIVES

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 53, No 8, Aug 83
(manuscript received 21 Feb 82) pp 1701-1706

MEL'NIKOV, N. N., RAZVODOVSKAYA, L. V., ENGLIN, V. M., KARASEVA, T. A., GOLOVKIN, G. V., BOGEL'FER, L. Ya., NEGREBETSKIY, V. V. and GRAPOV, A. F., All-Union Scientific Research Institute of Chemical Means of Plant Protection, Moscow

[Abstract] Studies were undertaken on the phosphorylation and thiophosphorylation of 3-amino-1,4-benzothiazines which showed that reaction of phosphorus acid chlorides with 3-imino-2,3-dihydro-4H-1,4-benzothiazine in chloroform at 50-60°C in the presence of triethylamine led to the formation of phosphorylated products that were rapidly hydrolyzed and on storage formed the corresponding salts. Furthermore, both the phosphoryl- and the thiophosphoryl-derivatives are essentially inert in reactions with electrophilic reagents and fail to react even with arylisocyanates. The 2-amino-1,4-benzothiazines possess dual reactivity and the structures of the products were based on tabulated IR, NMR, and mass-spectroscopic data. References 9: 6 Russian, 3 Western.

[24-12172]

UDC 547.26'118

UNUSUAL REACTIVITY OF DIALKYLACETYL DITHIOPHOSPHITES WITH ACYL HALIDES AND ACIDS

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 53, No 8, Aug 83
(manuscript received 15 Jul 82) pp 1706-1713

SINYASHIN, O. G., KOSTIN, V. P., BATYYEVA, E. S., PUDOVIK, A. N. and IVASYUK, N. V., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] The reaction mechanisms of the interaction of S,S-dialkylacetyl dithiophosphites with acyl chlorides may theoretically involve either the formation of α -acetyl dithiophosphonates via the Arbuzov rearrangement or, alternatively, the thioalkyl group may undergo replacement by a Cl atom. Experimental studies with S,S-diethyl- and S,S-dipropylacetyl dithiophosphites demonstrated that in reactions with acetic, trichloroacetic, or benzoic acid chlorides the Arbuzov rearrangement does not occur but that the acetoxy group is replaced by Cl. Acid catalysts were found to enhance the reaction 11- to 30-fold, depending on the reactants, while the addition of a base slowed the reactions two- to three-fold. References 20: 17 Russian, 3 Western.

[24-12172]

UDC 547.241

ISOMERIZATION OF P(III) THIOESTERS IN PRESENCE OF HALOSILANES

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 53, No 8, Aug 83
(manuscript received 14 Sep 82) pp 1713-1715

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[Abstract] Studies on the isomerization of P(III) acid thioesters were carried out by the addition of trimethyliodo- and trimethylchlorosilane, which showed that S-ethylidiphenyl thiophosphinite, S-ethyl-ethylphenyl thiophosphinite, and triethyl trithiophosphate fail to react with trimethylhalosilanes at room temperature. However, at 100°C the phosphinites reacted with trimethyliodo-silane to give the corresponding phosphine sulfides identified on the basis of NMR and ESR spectra. The formation of the phosphine sulfides was ascribed to donor-acceptor interactions between the sulfur and silicon atom with formation of an intermediate sulfonium compound and its subsequent stabilization. The process of isomerization was accompanied by limited formation of phosphonium iodides. References 7: 3 Russian, 4 Western.

[24-12172]

UDC 547.241+547.657.+547.689

PHOSPHORYLATION OF CERTAIN ORGANIC LUMINOPHORES

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 53, No 8, Aug 83
(manuscript received 28 Sep 82) pp 1718-1720

KOMLEV, I. V., TAVRIZOVA, M. A., KHROLOVA, O. R. and MASTRYUKOVA, T. A.,
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Moscow

[Abstract] 3-Aminobenzanthrone (emitting in the orange-red region) and N-phenyl-4-aminonaphthalimide (emitting in the green part of the spectrum) were subjected to chemical modification in an attempt to secure improved luminophores. Replacement of one hydrogen atom of the amino group by a phosphorylmethyl group in the case of 3-aminobenzanthrone led to hypsochromic shifts in the adsorption and emission spectra of the derivative, and intensification of emission in comparison with 3-aminobenzanthrone. In addition, the alpha-phenylphosphorylmethyl derivative of 3-aminobenzanthrone showed improved photostability over the parent compound. A similar modification of N-phenyl-4-aminonaphthalimide had no marked effects on absorption or emission characteristics, and failed to affect the rate of photodecomposition. References 5 (Russian).

[24-12172]

UDC 543.422:547.1'113

ELECTRON DONOR AND ACCEPTOR FUNCTIONS OF PHYSIOLOGICALLY ACTIVE AND MODEL COMPOUNDS, PART 4: PHOSPHINATES, PHOSPHONATES AND PHOSPHATES

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 53, No 8, Aug 83
(manuscript received 27 Nov 81) pp 1720-1724

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[Abstract] Evaluation of the electron donor factor (E) of 86 phosphinates, phosphonates and phosphates with 1, 2 or 3 alkoxy or aroxy groups demonstrated that the values of E ranged from 0.9 to 1.2, and were largely determined by noninductive intramolecular interactions. The upper values of E were characteristic of trimethyl phosphate and diaryl phosphonates, while the lower limit was set by alkyldialkyl phosphinates. In terms of electron donor function these compounds are equivalent with simple dialkyl esters. The experimental aspects of this study have been published previously [Rayevskiy, OA, et al., ZH. OБSHCHEY KHIMII, 48:1053(1978)]. References 7 (Russian).
[24-12172]

UDC 547.216'18

PHOSPHORYLATED NITROGENOUS HETEROCYCLIC COMPOUNDS, PART 9: PHOSPHONOALKYLATED IMIDAZOLES

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 53, No 8, Aug 83
(manuscript received 5 Oct 82) pp 1729-1734

MATEVOSYAN, G. L. and ZAVLIN, P. M., Leningrad Agricultural Institute

[Abstract] Interest in the biological properties of phosphorylated imidazoles led to studies on the synthesis of phosphonoalkylated imidazoles with the substituent occupying position 1. N^1 -phosphomethylated imidazole was prepared by reacting imidazole with phosphorous acid and formalin in the presence of HCl. Phosphonoethylated imidazole was obtained by the reaction of imidazole with di(beta-chloroethyl)vinylphosphonic acid ester; if the latter reaction was carried out in the presence of $AlCl_3$, imidazole was added to the vinyl group of the ester by nucleophilic addition. Bis-hydrochlorides of di(beta-1-imidazolylethyl)beta-(1-benzimidazolylethane)phosphonate were synthesized by the reaction of imidazole with di(beta-chloroethyl)-beta-(1-benzimidazolyl)-ethyl phosphonate. A total of 12 compounds were synthesized, the structures of which were confirmed by IR and UV spectroscopies. Figures 1; references 12: 10 Russian, 2 Western.
[24-12172]

UDC 547.484.34'118

PHOSPHORYLATED THIOACETOACETIC ESTER

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 8, Aug 83
(manuscript received 27 Aug 82) pp 1734-1739

SMIRNOVA, T. V., KOZENASHEVA, L. Ya. and KURKOVSKAYA, L. N., Moscow Institute of Chemical Technology imeni D. I. Mendeleyev

[Abstract] Studies on the reaction of thioacetoacetic ester and its sodium salt with phosphoryl chlorides showed that the former underwent phosphorylation with the formation of S-vinyl phosphates in the presence of triethylamine and inert organic solvents (benzene, diethyl ether, dioxane) at 20-80°C. PMR spectra demonstrated that in the presence of triethylamine the cis-enthiol form of thioacetoacetic ester was transformed into the reactive trans configuration which then underwent phosphorylation to the trans-enthiolphosphate isomers. A similar reaction sequence applies to acetoacetic ester. The sodium salt of thioacetoacetic ester undergoes phosphorylation with the formation of a mixture of cis and trans isomers of enthiolphosphates, while phosphorylation of the sodium salt of acetoacetic ester results in the formation of only the cis isomer of the corresponding enolphosphate. Addition of the phosphoryl group to the sulfur atom was confirmed by IR and NMR spectroscopies and mass spectrometry. References 13: 4 Russian, 9 Western.

[24-12172]

UDC 547.567+546.131

PCl_3^+ . RADICALS IN REACTIONS OF O-QUINONES WITH PHOSPHORUS TRICHLORIDE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 8, Aug 83
(manuscript received 14 Jul 82) pp 1739-1742

KLIMOV, Ye. S., BUMBER, A. A. and OKHLOBYSTIN, O. Yu., North Ossetian State University imeni K. L. Khetagurov

[Abstract] In view of the contradictory data on the reaction mechanisms between organophosphorus compounds and quinones, studies were conducted on the reaction of phosphorus trichloride with o-chloranil, 9,10-phenanthrenequinone, 4,6-di-tert-butyl-1,2-benzoquinone, and alphanaphthoquinone. Over a temperature range of -60 to -30°C the course of the reaction in toluene was indicated by a color change to green and ESR signals indicating the formation of paramagnetic particles. Above -30°C the reaction mixture became colorless and the ESR signals disappeared. Analysis of the ESR spectra demonstrated that phosphorus containing cation radicals are formed as intermediate products and that their subsequent interactions lead to the formation of trichlorophosphorane derivatives. Voltamperograms derived from oxidation of PCl_3^+ in acetonitrile

and dimethylformamide indicated that the first stage in the oxidation involved formation of the unstable radical (PCl_3^+). Figures 1; references 8: 6 Russian, 2 Western.

[24-12172]

UDC 547.241

REACTION OF PERFLUOROIODOALKANES WITH P(III) ACID ESTERS: PART 6: SYNTHESIS
OF TRIFLUOROMETHYL AND HEPTAFLUOROPROPYL PHOSPHONATES

Leningrad ZHURNAL OБSHCHEY KHMII In Russian Vol 53, No 8, Aug 83
(manuscript received 4 Nov 82) pp 1743-1745

SHIBAYEV, V. I., GARABADZHIU, A. V. and RODIN, A. A., Leningrad Technologic Institute imeni Lensoveta [Leningrad Soviet]; Leningrad Sanitary-Hygienic Institute

[Abstract] Conditions are described for the synthesis of trifluoromethyl and heptafluoromethyl phosphonates by the reaction of perfluoroiodoalkanes with triisobutyl phosphite, with the products identified by NMR spectroscopy and synthetic behavior because of their thermal instability. The thermal instability of the perfluoroalkyl phosphonates was ascribed to the weakness of the R_F-P bond, since the presence of electron acceptor groups on P (e.g., fluoroalkyls) diminishes the extent and diffusion of the d-orbitals and enhances their overlap with the π -electron cloud. Replacement of even one alkoxy group in trialkyl phosphites with an alkyl group leads to a pronounced +I effect responsible for stabilization of the R_F-P bond. References 8: 6 Russian, 2 Western. [24-12172]

UDC 541.124:54-39:546.183.5

REACTION OF SILICON SUBGROUP HETEROORGANIC PEROXIDES WITH PHOSPHATES AND PHOSPHITES

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 53, No 8, Aug 83
(manuscript received 24 Dec 82) pp 1752-1755

GORBATOV, V. V., YABLOKOVA, N. V., ALEKSANDROV, Yu. A. and IVANOV, V. I., Scientific Research Institute of Chemistry, Gorki State University imeni N. I. Lobachevskiy

[Abstract] The mechanism of action of heteroorganic peroxide decomposition by phosphorus compounds was studied in a system employing organosilicon and organotin peroxides, and phosphates and phosphites as the electron donors leading to decomposition. Using a four- to eight-fold donor excess in nonane or anisole the reactions involving phosphates followed first order kinetics and those with phosphites second order kinetics (first order with respect to each component). Furthermore, the reactions with phosphates involved complex formation which was responsible for peroxide activation and facilitated O-O bond homolysis. Reactions with the phosphites involved nonradical S_N^2 oxidation of the phosphite by the peroxide or a radical mechanism in the peroxide-phosphite complex with one electron phosphite oxidation. The second reaction mechanism was confirmed by the effects of inhibitors and initiation of radical polymerization of butylmethacrylate. References 13: 8 Russian, 5 Western. [24-12172]

UDC 547.869.2'118

3-THIOCYANOPHENOTHIAZINE DERIVATIVES, PART 1: SYNTHESIS AND PHOSPHORYLATION
OF 3-THIOCYANO-10-HALOACYLPHENOTHIAZINES

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 53, No 8, Aug 83
(manuscript received 2 Dec 82) pp 1755-1757

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Academy of Sciences

[Abstract] 3-Thiocyanato-10-haloacetylphenothiazines were synthesized by the reaction of 3-thiocyanophenazine with haloacetyl halides. Specifically, 3-thiocyanato-10-chloroacetylphenothiazine was obtained by reaction with chloroacetyl chloride, and 3,7-dithio-10-chloroacetylphenothiazine by the reaction of 3,7-dithiocyanophenothiazine with the same halide. Phosphorylation of 3-thiocyanato-10-chloroacetylphenothiazine with triethyl phosphite could follow two reaction mechanisms. Mixing of both components in equimolar concentrations and moderate heating led to a violent reaction with the production of ethyl cyanide odor and partial consumption of the chloroacetyl group. Heating of a mixture in which the components were in a 1:2 ratio resulted in phosphorylation of both reactive sites after 4 h, as indicated by NMR signals corresponding to a phosphonate and monothiophosphate group. References 5: 1 Rumanian, 2 Russian, 2 Western.

[24-12172]

UDC 547.819/822.3/811

SYNTHESIS OF BIHETEROCYCLIC KETOPHOSPHORINANES

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 53, No 8, Aug 83
(manuscript received 19 Nov 82) pp 1757-1763

ISAYEVA, G. M., BUTIN, B. M., IL'YASOV, R. N. and YERZHANOV, K. B., Institute of Chemical Sciences, Kazakh SSR Academy of Sciences, Alma-Ata

[Abstract] Studies were conducted on the synthesis of biheterocyclic keto-phosphorinanones in order to provide additional substrates for further stereochemical studies on heterocyclic compounds and because many such compounds based on N- and O-containing heterocycles possess physiological activity. Seven phosphabicyclodecanones were prepared by the cycloaddition reaction involving 1-methyl-4-(3-diethyl-amino-1-oxo)propyl- Δ^3 -dehydropiperidine and 2,2,-dimethyl-4-(3-diethylamino-1-oxo)propyl- Δ^4 -dihydropyran with phenylphosphine. The bicyclic phosphadecanones were capable of undergoing oxidation by the oxygen in the air and also added sulfur and selenium to give the corresponding derivatives containing phosphoryl, thio- and seleno-phosphoryl groups. References 18: 10 Russian, 8 Western.

[24-12172]

UDC 547.491.6

DITHIOPHOSPHATE GROUP MIGRATION IN N-ALKYL-N'-ARYLCARBODIIMIDES

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 53, No 8, Aug 83
(manuscript received 22 Nov 82) pp 1763-1767

FETYUKHIN, V. N. and VOVK, M. V., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Studies on tautomeric transformations in α -dithiophosphate substituted alkylisocyanates led to the observation that N-alkyl-N'-arylcarbodiimides undergo irreversible anionotropic rearrangement with migration of the dithiophosphate group at 25°C in benzene with formation of diazadienes. The susceptibility of these carbodiimides to isomerization into the corresponding diazadienes is largely determined by the nature of the substituent on the cumulene nitrogen atom. Aromatic substituents facilitate and stabilize the resultant diazadienes, which are colorless crystalline or viscous substances readily soluble in most organic solvents. On reaction with water the diazadienes yield the corresponding S-phosphorylated isothioureas.

References 6: 2 Russian, 4 Western.

[24-12172]

UDC 547.887.3

PHOSPHORYLATED 1,1-DIPHENYLHYDRAZYL RADICALS

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 53, No 8, Aug 83
(manuscript received 5 Jul 82) pp 1767-1775

KORNUTA, P. P., BOBKOV, V. N., POLUMBRIK, O. M. and MARKOVSKIY, L. N., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Phosphorylated derivatives of 1,1-diphenylhydrazine were studied to evaluate the effects of phosphorus-containing groups on the density distribution of the unpaired electron in the P-N-N triad on the stability 1,1-diphenylhydrazyl radicals. On the basis of the oxidation data and the ESR signals the hydrazyls were ranked in terms of stability at room temperature in benzene or dioxane, and the a_N^{α} , a_N^{β} , and a_P constants were approximately of equal value. This fact indicates that the phosphorus-containing group has a pronounced effect on the delocalization of the unpaired electron along the N-N bond. Figures 2; references 21: 14 Russian, 7 Western.

[24-12172]

UDC 547.118'26

REACTIVITY OF PHOSPHORUS-CONTAINING DISULFIDES: REACTION OF BIS(DIISOPROPOXY- AND DIPHENYLTHIOPHORYL) DISULFIDES WITH ANILINE AND m-PHENYLENEDIAMINE

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 53, No 8, Aug 83
(manuscript received 30 Nov 82) pp 1775-1778

KHASKIN, B. A., TORGASHEVA, N. A. and NEGREBETSKIY, V. V., All-Union Scientific Research Institute of Chemical Means of Plant Protection, Moscow

[Abstract] The reactivity spectrum of phosphorus-containing disulfides was expanded by studies on the reaction of bis(diisopropoxy- and diphenylthiophoryl) disulfides with aniline and m-phenylenediamine. Reaction of these disulfides with aniline in sealed ampules at 90-100°C for 20 h resulted in the formation of 0,0-diisopropylthiophosphorylsulfene-N-phenylamide and 0,0-diisopropyl-N-aminophenylidithiophosphate. By means of reaction with m-phenylenediamine in benzene at 80°C the corresponding S-diaminophenyl dithiophosphates or phosphinates were synthesized. The structures of the products were confirmed by PMR data and their reactions with 4-chloro- and 3,4-dichlorophenylisocyanate to form the corresponding phosphorus bis-ureas.

References 2 (Russian).

[24-12172]

UDC 547.(245+241)

SILICON-CONTAINING AMMONIUM AND PHOSPHONIUM SALTS

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 53, No 8, Aug 83
(manuscript received 19 Nov 82) pp 1831-1834

BROVKO, V. S., SKVORTSOV, N. K., IVANOV, A. Yu. and REYKHSFEL'D, V. O.

[Abstract] Details are presented on the synthesis, physicochemical characteristics and proton shift signals of silicon-containing phosphonium and ammonium salts. The salts were prepared by quaternization of ω -halogen substituted alkylsilanes and had the general formula $R'R_2^2Si(CH_2)_nER'Hg$, where $R' = Me$ or EtO , $R'' = Me$ or MeO , $E = N$ or P , $R = Me$, Et , Ph , or Bu , and $n = 1$ or 3 . In addition, similar salts were prepared by hydrosilylation of phosphonium salts with an unsaturated radical on the phosphorus atom. References 12: 6 Russian, 6 Western.
[24-12172]

UDC 547.341

REACTION OF CYCLIC TRIMETHYLSILYL PHOSPHITES WITH BENZIL

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 53, No 8, Aug 83
(manuscript received 15 Dec 82) pp 1923-1924

OVCHINNIKOV, V. V., YEVSTAF'YEV, Yu. G., CHERKASOV, R. A. and PUDOVIK, A. N., Kazan State University imeni V. I. Ul'yanov-Lenin

[Abstract] Cycloaddition products were obtained by the reaction of 2-trimethylsiloxy-4,5-dimethyl-1,3,2-dioxaphospholane and 2-trimethylsiloxy-4,5-benzo-1,3,2-dioxaphospholane with benzil. The former reaction was highly exothermic and occurred at -50 to -40°C, whereas the latter required heating to 40-50°C. The products were stable for several days at room temperature in toluene or p-xylene, but on heating for several hours at 70-80°C underwent transformation into silylated cyclophosphates. References 6: 3 Russian, 3 Western.

[24-12172]

UDC 547.341

PHOSPHORYLATION OF TETRAHYDROPYRAN DERIVATIVES

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 53, No 8, Aug 83
(manuscript received 14 Feb 82) pp 1924-1925

FRIDLAND, S. V. and LAPTEVA, L. I., Kazan Institute of Chemical Technology imeni S. M. Kirov

[Abstract] The effects of ethyl and phenyl substituents at position 2 of tetrahydropyran on the course of its phosphorylation were investigated in reactions carried out in benzene with PCl_5 . Chemical analysis of the products and PMR spectra showed that phosphorylation involved the formation of phosphinates in which the dichlorophosphine group is added to the C^5 atom, giving the dichlorides of 2-ethyl- and 2-phenyl-5,6-dihydropyran-5-phosphinates. References 1 (Russian).

[24-12172]

UDC 547.558.1+547.656

REACTION OF HALOMETHYLNAPHTHOQUINONES WITH TRIPHENYLPHOSPHINE

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 53, No 8, Aug 83
(manuscript received 21 Feb 83) pp 1925-1926

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[Abstract] Quinones containing halomethyl groups have been found to enter into nucleophilic reactions with halogen substitution and formation of phosphonium salts. The reactions proceed readily at room temperature in various solvents (best in benzene or toluene) from which the salts are precipitated. In this manner reaction of 2-bromomethylnaphthoquinone with triphenylphosphine yielded [(1,4-naphthoquinonyl-2)methyl]triphenyl phosphonium bromide, and [(3-methyl-1,4-naphthoquinonyl-2)methyl]triphenyl phosphonium bromide was obtained in an analogous manner. References 4: 1 Russian, 3 Western.
[24-12172]

UDC 547.558.1

PYRAZOLE-, ISOXAZOLE- AND TRIAZOLE- PHOSPHONIUM SALTS

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 53, No 8, Aug 83
(manuscript received 9 Dec 82) pp 1926-1927

MEGERA, I. V., Chernovtsy State Medical Institute

[Abstract] In view of the importance of phosphonium salts in the synthesis of heterocyclic compounds, a convenient method was developed for the preparation of phosphonium salts containing pyrazole, isoxazole, and triazole moieties. 3-Isoxazolylmethyltriphenylphosphonium chloride was obtained by the reaction of 3-chloromethylisoxazole with Ph_3P in chloroform for 40-50 h. The product was obtained by filtration of the sediment. 3-Pyrazolylacetyltriphenylphosphonium chloride was obtained by the reaction of chloromethyl-pyrazolyl-3-ketone with $(\text{C}_6\text{H}_5)_3\text{P}$ in chloroform after 10 h of heating and extraction with small aliquots of ether. Triazole phosphonium salts were obtained in almost quantitative yields by the reaction of 1-aryl-4-chloroacetyl-1,2,3-triazoles with $(\text{C}_6\text{H}_5)_3\text{P}$ in chloroform. References 9: 1 Russian, 8 Western.
[24-12172]

PESTICIDES

FAILURES IN CONSTRUCTION OF NEW PESTICIDE PLANT

Baku VYSHKA in Russian 2 Oct 83 p 2

[Article by G. Rzayev, deputy chief of the capital construction department of the "Khimprom" [Chemical Industry] Association; K. Rustamov, brigade leader of the "Azstal'konstruktsiya" [Azerbaijan Steel Structures] Construction and Installation Administration; and S. Gopanyuk, VYSHKA correspondent: "On the Brink of Failure"]

[Text] A complex for the production of lindane is being erected at the Sumgait "Khimprom" [Chemical Industry] Association. This preparation is used for the chemical protection of agricultural crops against harmful insects. In contrast to poisonous chemicals used for similar purposes that have been taken out of production, lindane does its work and then is completely degraded; it does not pollute the natural environment. As we can see, the national economy is in great need of this progressive material and there is a great demand for it. In order to satisfy the demand, a decision was made to organize production of lindane and considerable resources were allocated for this purpose.

The client--"Khimprom"--and the general contractor--Trust No 1 of the Ministry of Industrial Construction--are obligated according to the plan to put the project into operation by 31 December.

However, a discussion with I. Umudov, director of construction for "Khimprom"; M. Maksudov, chief engineer of Trust No 1; and other heads of subdivisions participating in the construction project, indicated that the project is on the verge of failing. The eight-month plan for construction and installation work has not been fulfilled. The goal was to complete work totalling 6.8 million rubles and only 5.3 million rubles' worth was completed. Very little of the construction work has actually been completed. Of the 10 main production buildings and projects, only one--building No 306--is ready for installation work; and it is not even totally ready. The general contractor is to blame for the fact that the chief installation workers who were called in at the end of August have still not started working.

By talking with brigade leaders and regular construction workers, and looking at the documents, we had to reach the conclusion that the general contracting trust, its Construction Administrations 18 and 12, and others put themselves into a difficult situation by the quality of their previous work on the project, and they set up the conditions for failure. The customer received all

the equipment back in 1980. The builders were well financed. But in 2 years the general contractor completed only half of the planned amount of construction and installation work. The general contractor was left with 11 million rubles' worth of work to complete in the last year alone. There is yet another fact here. M. Akhundov, chief of Construction Administration 18, reproached the chemists, saying that they are not releasing territory from the existing plant for new construction work.

I. Umudov said, "That's true, we are not releasing certain territory. There is an old pumping station located there for transferring products. Before we remove it, the builders need to erect building No 362 with a pump and other facilities. The deadline for its completion was 20 April. Did you finish it for us, comrade Akhundov?"

Akhundov had nothing to say. The building still is not ready today. This is how today's problems have come about.

A. Aliyev, Akhundov's assistant, entered the conversation. "Not everything is that bad. There was a major turn-around in September. We started working with a great sense of responsibility. A 10-day system for planning and reporting was introduced. We took on the job of fulfilling a plan that was double what had been accomplished in August."

It is fine that they took on this task, but the results have not been great. Over 2 10-day periods, instead of completing work valued at 667,000 rubles, they completed work valued at 506,000 rubles. The results are even worse at the Azerbaijan "Stal'konstruksiya" [Steel Structures] Construction and Installation Trust, which is engaged in the erection of buildings made of reinforced concrete and metal. The entire construction project depends on the pace of its work. In September the Construction and Installation Trust was supposed to complete installation work valued at 312,000 rubles. As of 21 September, 120,000 rubles' worth had been completed.

In the remaining days of the month, the installation workers were able to complete another 40,000-50,000 rubles' worth of work, not more. That means that only half the plan was fulfilled.

What is the reason for these regular failures?

Directors of the contracting organizations have explained the failure to fulfill the plan as a result of a shortage of manpower at all levels. With the help of the Sumgait city party committee and the chemists themselves, more people were sent to the construction site than provided for in the estimates, in order to fulfill the plan for September. The plan called for 515 people, and 570 were sent. But in the second shift, there were only 72. In other words, the plan was not fulfilled even with a large number of workers. Thus, the reason does not lie in a manpower shortage, but in the organization of labor at the construction site.

The remarks made by comrade Yu. V. Andropov at a meeting between the CPSU Central Committee and veterans of the party are quite fitting here. He said that in some places the call for strengthening discipline has been interpreted

as nothing more than strict administrative control over the presence of each person at his work site from the beginning of his shift to the end. But it is far from everywhere that there is concern over what a person does at his work site, how he handles his assignments, and whether the necessary conditions have been created for productive labor.

Having visited various sections at the construction site, we came away convinced that production discipline there is extremely slack. We can give an example. Machinery operators from Construction and Installation Administration No 2 of the "Promstroymekhanizatsiya" [Industrial Construction Mechanization] Trust were given an assignment. They were to prepare the foundation holes for the electric power line supports. But it was discovered that one of the supports had to be placed right at the bus stop near "Khimprom".

It took the client many days to resolve this problem. The result was that they missed the deadline for fulfilling the plan.

We can cite another case. Part of the installation workers from the "Stal'konstruktsiya" Construction and Installation Administration were standing around idle. What was the delay? One of the workers answered: "We don't have any structures to work with. They weren't delivered." But the construction site was strewn with metal and reinforced concrete pieces to be used in erecting the building. It was a strange situation. The structures were there, but at the same time it seemed as if they were not there. During 2 10-day periods in September over 300 cubic meters of reinforced concrete and 131 tons of metal items were delivered but not installed. We asked the section chief, Sh. Shukyurov for an explanation.

"There is nothing strange about it," Shukyurov answered. "Figuratively speaking, they brought us a roof, but nothing to support it. Because of a shortage of just 5 beams we cannot start installing the 160 slabs of covering material that you see lying at the construction site. Who is to blame? Our general contractor and N. Ismailov, director of the "Zhelezobeton" [Reinforced Concrete] Trust. The general contractor does not try to coordinate production of articles that will be consistent with the installation process. The "Zhelezobeton" Trust finds it convenient to fulfill the plan for concrete slabs, but not for beams and other support elements. What is convenient for them ends up causing us grief."

Also deserving of criticism is the work of the Sumgait Metal Structures Plant of the "Azneftekhimmontazh" [Azerbaijan Petrochemical Installation] Trust; the director is V. Pauker. He did not provide the complete set of metal beams needed for building No 303, which is delaying the work not only of the installation workers, but also the construction workers of Construction Administration 18 who are supposed to do the concrete work after the installation workers have finished their jobs.

An outsider attending the last meeting of the lindane plant construction staff would have been surprised by the following fact: The "Azstal'konstruktsiya" Construction and Installation Administration, Construction Administration 13, and 5 other organizations involved failed to meet the goal for building No 413.

This report did not seem to alarm anyone. It was not followed by any penalties and there were not even any verbal reprimands.

The complacent attitude of the directors of Trust No 1, the Ministry of Industrial Construction, and other organizations toward their undisciplined section leaders was explained to us one day during the last 10 days of September when we visited the construction site. At almost all the sections dozens of machines and hundreds of workers were standing idle.

We went up to one of the groups that was "resting". A. Bannikov, an installation worker, and I. Sobolev, a crane operator, from "Stal'konstruktsiya" were both half-lying down on a slab that was ready to be raised.

"What's the delay?"

"There's no electricity. We can't weld the structure at the top."

Their chief, S. Shukyurov, came up and explained that at 10 o'clock in the morning the electrical supply for the entire construction site had been turned off. Something had happened where the power is turned on at the chemical plant substation that supplies electricity to the construction site. The electricians had to be found, the problem had to be repaired...The power was restored only at the end of the shift. The work day of over 500 people at this important construction project was irretrievably lost. According to the construction workers, interruptions in the electrical supply due to problems in the transformer occur quite frequently. M. Maksudov and M. Akhundov blame the chemists for this. But really, a great deal of the blame belongs to the general contractor. The general contractor should have set up a temporary substation at the construction site. The Trust managers thought that they would save by hooking up to the chemical plant. But as we can see, this "saving" caused immense losses.

This and the other miscalculations described above point to one thing: Since the first days of construction, the general contractor has not taken a serious approach to the work and has ignored the project's preparation stage. Now all this is taking its toll on plan fulfillment and on everyone's nerves. The directors of the construction project cannot fail to understand their guilt and the miscalculations that they have allowed, because it is due to these mistakes that their subordinates are now failing to carry out their assignments. Therefore they cannot hold their subordinates responsible.

There are no problems that cannot be corrected. In spite of the difficulties, in September the rate of work at the construction site increased. There is a possibility, by making an intense effort, to meet the goal for putting the lindane plant into operation. There is still a whole quarter of the year left. Reserves must be utilized, however.

Where are the reserves, though? We already mentioned that of 570 people, only 72 were working the second shift, and none of them were involved in the most important work. Putting 200 people in the second shift would double the amount of work done. Another reason for doing this is that having so many people in

the first shift does not lead to an increase in labor productivity; it has just the opposite effect. This indicator dropped by almost 15 percent. Not everyone has a large enough work area, enough materials or machinery. Lack of preparation on the part of the general contractor also makes it difficult to organize a full second shift. The vast territory of the construction site is not illuminated, the excavations and holes in the floors are not fenced off. Frankly, it is not totally safe to walk around here during the day. The general contractor can and should prepare the necessary conditions for the second shift. This is one of its responsibilities. The subcontractors and the client should not take a strictly formal approach to this issue either. They need to join forces and create safe working conditions in the sections; they should provide lighting and services for the workers. Then the workers will agree to work the second shift without putting up long arguments.

In other words, this important issue must be resolved jointly, because the responsibility for plan fulfillment is shared by everyone.

9967
CSO: 1841/14

PETROLEUM PROCESSING TECHNOLOGY

UDC 661.66.041.001.24

EXPERIENCE IN OPERATION OF REACTION TUBES IN NATURAL GAS CONVERSION FURNACES

Kiev KHMICHESKAYA TEKHNOLOGIYA in Russian No 5, Sep-Oct 83
(manuscript received 7 May 82) pp 34-36

KADYGROV, L. A. and STEPANOV, A. V., Institute of Gas, Ukrainian SSR
Academy of Sciences

[Abstract] This article shares the experience in the operation of commercial tube natural gas conversion furnaces based on analysis of furnace operation characteristics obtained during the course of long-term operation of the Kellogg and Foster-Wheeler furnaces. Technological characteristics of operation of the tube furnaces in the stage of vapor reforming and the dynamics of change in maximum tube temperature over the course of long-term operation of the furnaces are presented in tabular form. The analysis of the operation of the furnaces shows that the reliability of their operation depends to a great extent on the reliability of operation of the reaction tubes themselves. Uneven heating of the tubes, formation of cavities in the catalyst layer or feeding of moist steam for conversion causes accelerated failure of the tubes. Proper utilization significantly increases the service life of reaction tubes.

References 5: 4 Russian, 1 Western.

[36-6508]

PHARMACOLOGY AND TOXICOLOGY

UDC 615.283.929:547.831.4].015.4:612.111.11

STUDY OF MECHANISMS OF ANTIMALARIAL ACTION OF CHLOROQUINE AND DABEQUINE:
FORMATION OF COMPLEXES WITH HEMIN

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 17, No 8, Aug 83
(manuscript received 15 Feb 83) pp 903-907

GRINBERG, L. N. and LUKMANOVA, N. E., Institute of Medical Parasitology and Tropical Medicine imeni Ye. I.Martsinovskiy, USSR Ministry of Health, Moscow

[Abstract] Spectrophotometric and nephalometric studies of complex formation of hemin with chloroquine and dabequine were performed to try to discover the nature of the antimalarial action of these drugs. Chloroquine and dabequine interacted only with molecular forms of hemin. The drugs formed a complex with hemin and promoted its aggregation; both drugs interacted with hemin in a similar manner but dabequine reacted to a greater degree than did chloroquine. It was assumed that the most probable receptor, responsible for accumulation of chloroquine and other antimalarial drugs with a similar mechanism of action in the cell, is ferrihem, as a precursor or component of hemozoin. The results obtained indicate that formation of aggregated forms of hemin in the presence of chloroquine and dabequine is one of the stages of the antimalarial action of these compounds. Chemical aspects of interaction of the complex-forming substances were discussed. Figures 4; references 14: 5 Russian, 9 Western.

[22-2791]

UDC 615.276.2.033.36

STUDY OF CUMULATIVE PROPERTIES AND DISTRIBUTION OF A NEW IMMUNODEPRESSIVE COMPOUND

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 17, No 8, Aug 83
(manuscript received 27 Jul 82) pp 908-911

ARIPOV, U. A., SAKHIBOV, A. D., KASYMOV, B. Z., ZIYAYEV, Kh. L., BIKTIMIROV, L., BARAM, N. I. and ISMAILOV, A. I., Tashkent Medical Institute; Institute of Bioorganic Chemistry, UzSSR Academy of Sciences, Tashkent

[Abstract] Cumulative properties of a new Soviet immunodepressor (disodium salt of 1,1',6,6'-tetraoxy-3,3'-dimethyl-5,5'-diisopropyl-7,7'-dioxy-2,2'-dinaphthalene-8,8'-dimethyleniminoethanesulfoxylic acid) were studied at the

Tashkent Medical Institute. A study of the pharmacokinetics of the ¹⁴C-labelled compound after daily injections in mice for four days showed its uneven distribution in the animal body, with maximum accumulation in the liver, prolonged stay of the radioactive products in the spleen and thymus, considerable residual radioactivity in many organs after a single intraperitoneal dose and slow excretion of the drug and (or) its metabolites from the body. A linear dose dependence of incorporation of radioactivity in the organs after increasing doses of the drug was established. Study of the level of the drug in subcellular fractions of liver cells showed its accumulation, basically, in mitochondrial and microsomal fractions. Sequential extraction of lipids, RNA and DNA from a homogenate and subcellular fractions of the liver cells and blood plasma showed that the drug and (or) its radioactive metabolites are bound, basically to lipids and proteins of the plasma and subcellular structure. Figures 2; references 9: 7 Russian, 2 Western.
[22-2791]

UDC 615.849.1.015.25:547.568

RADIOPROTECTIVE PROPERTIES OF SOME N-SUBSTITUTED 1-M-HYDROXYPHENYL-2-AMINOETHANOLS

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 17, No 8, Aug 83
(manuscript received 7 Jul 82) pp 922-925

ALPATOVА, T. A., KULINSKIY, V. I. and YASHUNSKIY, V. G. Krasnoyarsk Medical Institute

[Abstract] Analogs of mesathone containing other alkyl and aralkyl substituents instead of a methyl group at the nitrogen atom and a carbomethoxy group were synthesized and studied. The acute toxicity and radioprotective activity of the substances were studied after injection into female CBA mice and CAB X C₅₇BL/F₁ hybrid mice. The toxicity of the substances increased with the increase in volume of the alkyl substituents at the nitrogen atom and the compounds displayed virtually no radioprotective properties. References 11: 5 Russian, 6 Western.
[22-2791]

POLYMERS AND POLYMERIZATION

UDC 678.01:534

DETERMINATION OF MODULUS OF ELASTICITY DURING FLEXURE OF ELASTIC AND SOLID POLYMERS

Moscow KAUCHUK I REZINA in Russian No 9, Sep 83 (manuscript received 20 Dec 82)
p 35

BABKIN, V. G. and YAROSLAVTSEVA, T. A.

[Abstract] Elasticity modulus of polymers is usually determined on large and expensive as well as complicated machines. The axial compression relaxometer VN-5305 is a small, simple and inexpensive instrument, but it is not suitable for determination of elasticity modulus of solid plastics. It was modified by adding a sample holder to adapt this instrument to the determination of solid polymers' modulus of elasticity during flexure. Figure 1; references 2 (Russian).

[20-7813]

UDC: 66.085.3/.5

RADIATION TREATMENT OF POLYETHYLENE AND POLYMETHYLMETHACRYLATE

Kiev KHMICHESKAYA TEKHNOLOGIYA in Russian No 5, Sep-Oct 83
(manuscript received 9 Aug 82) pp 27-29

KNIZHNIK, Ye. I., GORDIYENKO, V. P., IL'ENKO, R. Ye. and ONISKO, A. D., Institute of Nuclear Research, Ukrainian SSR Academy of Sciences; Institute of Physical Chemistry, Ukrainian SSR Academy of Sciences

[Abstract] The most promising method of improvement of the properties of polyethylene is filling with inorganic additives and subsequent treatment with ionizing radiation. Type 21006-075 high density polyethylene was filled with type A-175 aerosil (SiO_2), the rutile form of titanium dioxide and crushed glass type NMO-6, cast under pressure, then bombarded with accelerated electrons at 10 kGr/s in air, then heat treated at 403°K. Modified matrices withstood 60 to 70 cycles of molding of concrete and steam treatment without significant deterioration of adhesive properties and 100 to 120 cycles with no changes in dimensions. The radiation technology developed allows the production of large and unique outlines within decorative products and variation of the depth of deposition, volume, density of lines and configuration of the pictures molded. References 13: 11 Russian, 2 Western.

[36-6508]

UDC 677.494.675-96.021.12

STUDY OF PROPERTIES OF POLYCAPROAMIDE FIBERS MODIFIED BY SIMULTANEOUS
GRAFTING OF POLYACRYLONITRILE AND POLYMETHACRYLIC ACID

Kiev KHIMICHESKAYA TEKHNOLOGIYA in Russian No 5, Sep-Oct 83
(manuscript received 30 Jun 83) pp 29-31

PIMONENKO, N. Yu., DRUZHININA, T. V., GABRIELYAN, G. A. and BOYTSOVA, L. V.,
Kiev Technological Institute of Light Industry

[Abstract] Modified polycaproamide fibers containing graft polyacrylonitrile plus graft polymethacrylic acid were produced by successive introduction to the reaction solution, during the course of grafting, of acrylonitrile and methacrylic acid. This report outlines the results of studies of the properties of the polycaproamide fibers thus modified as well as fibers modified with polyacrylonitrile alone. The double modification process increases hygroscopicity and decreases specific volumetric electric resistivity. The dual modification process does not result in deterioration of the basic properties of the graft copolymers in comparison to modification with polyacrylonitrile alone. The combination of higher resistivity and hygroscopicity is valuable for the protection of textile consumer products. Figures 2; references 6 (Russian).

[36-6508]

UDC 678.54.046

DIFFUSION MECHANISM OF CURING AND STRUCTURE OF COMPOSITE MATERIALS
REINFORCED WITH CHEMICAL FIBERS

Leningrad ZHURNAL PRIKLADNOY KHMII in Russian Vol 56, No 9, Sep 83
(manuscript received 5 Dec 81) pp 2077-2082

STUDENTSOV, V. N., Saratov Polytechnic Institute

[Abstract] This work involves study of the influence of diffusion stages on the kinetics of chemical processes in mixtures of CD-20 synthetic epoxy resin, cured under the influence of polyethylene polyamine and agent SF-342A with several chemical fibers: cellulose-viscose, diacetate, triacetate, polyester-lavsan, polyamide-capron, polyacrylonitrile-nitron and polypropylene. The relationship of the kinetics of curing of the binders with the structure of the composite material is studied as well. The initiating influence of the chemical fiber leads to a decrease in concentration of uncured binder near the surface of the fiber, causing diffusion of oligomers from the volume of the binder towards the surface of the fiber. Diffusion of uncured resin toward the fiber becomes the limiting stage in the curing process as the frequency of cross links of the cured binder increases and the effective diameter of clumps of diffusion molecules increases. Filling of the fiber pores with liquid oligomer resin at high pressure occurs rather rapidly and cannot lead to the next stage of the curing process. Figures 3; references 7 (Russian).

[37-6508]

UDC 541.127:541.128:541.64:547.391.1'264

KINETICS OF BUTYL ACRYLATE POLYMERIZATION WITH PORPHYRIN-COBALT IN
INDUCTIVE PERIOD

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHMICHESKAYA in Russian No 9,
Sep 83 (manuscript received 7 Dec 82) pp 2036-2042

OGANOVA, A. G., SMIRNOV, B. R., IOFFE, N. T. and YENIKOLOPYAN, N. S.,
Institute of Chemical Physics, USSR Academy of Sciences, Moscow

[Abstract] Conditions are described for the study of radical polymerization kinetics of butyl acrylate in the presence of Co(II)-tetraphenylporphyrin (CoP) during the induction period, since CoP also acts as a classical inhibitor of chain elongation with late post-effects. Data obtained at 60°C with azobisisobutyronitrile initiator showed that during induction in the presence of CoP the concentration of macroradicals increases more rapidly than would be the case with an irreversible radical acceptor. This observation could not be ascribed to consumption of the initiator during the period of induction since that would only retard radical polymerization, and supports the view that CoP functions as a reversible inhibitor. Figures 5; references 11: 8 Russian.

3 Western.

[28-12172]

UDC 542.91:547.1'128

REACTION OF LITHIUM DIPHENYL PHOSPHIDE WITH MONOSILACYCLOBUTANES

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHMICHESKAYA in Russian No 9,
Sep 83 (manuscript received 4 Nov 82) pp 2125-2129

USHAKOV, N. V., VDOVIN, V. M., POZDNYAKOVA, M. V. and PRITULA, N. A.,
Institute of Petrochemical Synthesis imeni A. V. Topchiyev, USSR Academy of
Sciences, Moscow

[Abstract] Conditions are described for the reaction of 1,1-dimethyl-1-silacyclobutane and 1-methyl-1-m-tolyl-1-silacyclobutane with lithium diphenyl phosphide in tetrahydrofuran to determine the possible extent of cyclobutane polymerization as a result of ring opening. Ring opening was followed by the formation Si-P and C-Li bonds which favored further polymerization of the monosilacyclobutanes. However, the extent of ring opening with lithium diphenyl phosphide was less rapid than with organolithium compounds. Removal of lithium hydride results in chain breakage even at the initial stages of polymerization, with the formation of molecules with allyl groups on the Si atom. References 7: 5 Russian, 2 Western.

[28-12172]

UDC 541.183:539.612

INFLUENCE OF SURFACE MODIFICATION OF METALS UPON ADHESIVE PROPERTIES OF THE SYSTEM STEEL TYPE 3 PLUS COPOLYMER OF ETHYLENE AND VINYLACETATE

Moscow KOLLOIDNYY ZHURNAL in Russian Vol 45, No 5, Sep-Oct 83
(manuscript received 13 Apr 82) pp 1024-1026

CHERNIKOV, O. I., MITROKHINA, L. L. and KACHAN, A. A., Institute of Physical and Organic Chemistry and Coal Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Data are presented from a study of the adhesive properties of steel 3 with an ethylene-vinylacetate copolymer following modification of the surface of the steel with sodium alkylsulfonates with various carbon radical lengths. Modification was performed by adsorption of molecules of the surface-active agents onto the surface of the metal from aqueous solutions. A two-layer film 1 mm thick was produced by coextrusion, the upper layer made of low density polyethylene, the adhesive layer made of an ethylene-vinylacetate copolymer with 14% vinylacetate content. The metal surface was modified with aqueous solutions of sodium alkylsulfonates with various carbon radical lengths. It was found that the maximum adhesive strength in the system was achieved with a concentration of the modifying solution equal to the critical concentration for micelle formation for all members of the homologous series of surfactants studied, increasing with increasing radical length. Figure 1; references 6: 5 Russian, 1 Western.

[35-6508]

UDC 541.182.42:532.783.004.3

EFFECTS OF LIQUID CRYSTAL MICROENCAPSULATION CONDITIONS ON PROPERTIES OF MICROCAPTURE MEMBRANES

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHMICHESKAYA TEKHNOLOGIYA in Russian Vol 26, No 8, Aug 83 (manuscript received 4 Nov 82) pp 968-971

ZHELEZNOV, K. N., KLOPOV, V. I., INDEYKIN, Ye. A. and BEL'TSOV, B. I., Chair of Colloid Chemistry, Ivanovo State University; Ivanovo Institute of Chemical Technology; Yaroslavl Polytechnical Institute

[Abstract] Optimum parameters for the encapsulation of liquid crystals were investigated using natural polyelectrolytes to determine the effects of the condition of microencapsulation on the capsular membranes. Studies with gelatin (pH 4.80) and gum arabic (pH 1.23) capsules polymerized with formaldehyde under various values of pH showed that the highest quality capsules in terms of intended use (e.g., drug delivery) were those for which the micro-encapsulation process was completed at a pH of ca. 7. Completion of the process at that pH assured capsules of optimum strength for the intended use and minimum swelling. Figures 5; references 8: 4 Russian, 4 Western.

[31-12172]

UDC 541.15.66.095.25.678

SYNTHESIS AND POLYMERIZATION OF MONOMERIC QUATERNARY SALT N,N-DIMETHYL-AMINOETHYL METHACRYLATE WITH HALOALKYLS

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHMICHESKAYA TEKHNOLOGIYA in Russian Vol 26, No 8, Aug 83 (manuscript received 20 Oct 81) pp 981-983

MAKSUMOVA, A. S., UMAROVA, I. K., DZHALILOV, A. T. and KAPRIYELOVA, G. V., Polymer Problems Laboratory, Tashkent Polytechnic Institute imeni A. R. Beruni

[Abstract] N,N-dimethylaminoethyl methacrylate quaternary salts were prepared with propyl or allyl iodides and used as monomers for polymerization initiated by azoisobutyronitrile in various solvents (dimethylformamide, ethanol, dimethyl sulfoxide). The resultant polymers were prepared at relatively low temperatures (30-50°C) and represented highly viscous water-soluble polyelectrolytes; the viscosity was inversely related to the concentration of the polymer. These polyelectrolytes were also found to be effective flocculants and removed over 90% of dispersed heavy metal ferrocyanides from colloidal solutions in one hour. Figure 1; references 4 (Russian).

[31-12172]

UDC 541.64+539.25+543.422.4

POLYMERIZATION OF ACRYLATE OLIGOESTERS

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHMICHESKAYA TEKHNOLOGIYA in Russian Vol 26, No 8, Aug 83 (manuscript received 21 Jul 81) pp 984-986

FRENKEL', R. Sh., PUKHOVTSEV, Yu. V., KUZ'MINA, E. A. and DONSKOVA, E. N., Chair of Synthetic Rubber Technology, Volgograd Polytechnic Institute

[Abstract] Studies were conducted on the effects of various initiators on the structure and properties of acrylate oligoesters with three-dimensional cross-linking. Evaluation of the effects of the initiators dicumyl peroxide, di-(2-benzothiazolyl) disulfide, 2-mercaptopbenzothiazole, tetramethylthiuram disulfide, and N-cyclohexyl-2-benzothiazolylsulfenamide demonstrated that the course of polymerization was predicted on sol-gel relationships, and electron micrographs of the final product showed globular structures with various degrees of agglomeration. The dimensions of the aggregated complexes and the density of crosslinking were determined by the sol-gel parameters. With polymerization conducted at 150°C, the effectiveness of the initiators in decreasing the sol component ranked as follows: dicumyl peroxide > di-(2-benzothiazolyl) disulfide > 2-mercaptopbenzothiazole > tetramethylthiuram disulfide > N-cyclohexyl-2-benzothiazolylsulfenamide > no initiator. Consequently, through the selection of the appropriate initiator the characteristics of the final polymer can be controlled. Figures 1; references 6 (Russian).

[31-12172]

RADIATION CHEMISTRY

UDC 541.15:546.46-31

RADIATION PROCESSES IN OH-DOPED MAGNESIUM OXIDE MONOCRYSTALS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHMICHESKAYA in Russian No 9, Sep 83 (manuscript received 16 Nov 82) pp 1954-1961

SPITSYN, V. I., BARSOVA, L. I., ZYAZYULYA, I. I. and YURIK, T. K., Institute of Physical Chemistry, USSR Academy of Sciences, Moscow

[Abstract] IR and ESR spectroscopies were employed in studies on thermal and radiation processes in single MgO crystals doped with different concentrations of OH⁻ and cations (Fe, Cr, Mn, Cu, Ni, Al, Ca, Ba). In the OH-doped single MgO crystals the protons of the Mg(OH)₂ microphase showed the greatest thermal mobility, with mutual redistribution of protons between the microphase and internodes commencing at 400°K. The second region of proton mobility is represented by the region of migration of cationic vacancies at 700-900°K. Effects of gamma irradiation (Co-60) in the OH-doped MgO crystals can be divided into three successive phases, consisting of the formation V_{OH} centers at low absorbed doses, followed by proton diffusion from the V_{OH} centers on further irradiation, and formation of $V_{(OH)}_2$ centers and internodal protons.

At doses higher than 1000 Mrads the Mg(OH)₂ microphase appears at the expense of the $V_{(OH)}$ center and the H_i^+ . Consequently, radiation-induced diffusion of hydrogen atoms in MgO crystals is dependent on the concentration of the admixed cations, the concentration of OH⁻, the absorbed radiation dose, and the temperature of irradiation. Figures 5; references 11: 2 Russian, 9 Western.

[28-12172]

RUBBER AND ELASTOMERS

UDC 678.762.2-134.65:678.026.2

SYNTHESIS AND APPLICATION OF BUTADIENE-METHYLVINYLPYRIDINE LATEX WITH GLOBULAR HETEROGENEITY

Moscow KAUCHUK I REZINA in Russian No 9, Sep 83 (manuscript received 31 May 82) pp 4-6

SHMURAK, I. L., LASHKINA, E. D., DEDUSENKO, V. N. and RYSKINA, N. V., Omsk Plant of Synthetic Rubber, Scientific Research Institute of Tire Industry

[Abstract] Impregnated compositions based on a combination of butadiene-methylvinylpyridine latex (DMVP-10x) and butadiene-carboxyl latex (SKD-1) are widely used in tire industry. In an attempt to improve adhesion properties of these compositions, the effect of increased concentration of methylvinylpyridine links (MVP) near the surface of the DMVP latex was studied. Copolymerization of butadiene with MVP was carried out in two stages: initially, butadiene was polymerized up to 50-70% conversion, then MVP was added to the reaction mixture and copolymerization was continued until complete conversion was achieved. Thus-obtained latex showed intraglobular heterogeneity: central areas of these globules were deficient in polar MVP links, and the external areas were rich in them. The product used in tire production exhibited greater bonding strength than DMVP-10x with statistically distributed MVP links.
Figures 4; references 6 (Russian)
[20-7813]

UDC 678.763.2.031-13.678.029.34

NOVEL CARBOXYL-GROUP-CONTAINING CHLOROPRENE LATEX

Moscow KAUCHUK I REZINA in Russian No 9, Sep 83 (manuscript received 9 Aug 82) pp 6-8

GEVORKYAN, A. V., ASTVATSATRYAN, S. A. and KALANTARYAN, L. K., Scientific Production Organization "Nairit"

[Abstract] A new carboxyl-group containing copolymerized chloroprene latex was obtained with high colloidal stability. Solid films prepared from it had a high thermal stability and good resistance to freezing temperatures. The process involved acidic copolymerization of chloroprene with rosin which acted as a reinforcer and modified a number of colloidal-chemical properties of latex. Figures 2; references 7: 2 Russian, 5 Western.
[20-7813]

UDC 678.762.2

THERMOVULCANIZATION OF RUBBERS AND RESIN MIXTURES AT HIGH PRESSURES

Moscow KAUCHUK I REZINA in Russian No 9, Sep 83 (manuscript received 14 Jul 82)
pp 8-11

VINOGRADOV, G. V., GOVOROVA, O. A., FRENKIN, E. I. and PODOL'SKIY, YU. Ya.,
Institute of Petrochemical Synthesis imeni A. V. Topchiyev, USSR Academy of
Sciences, Scientific Research Institute of Rubber Industry

[Abstract] Properties of high pressure vulcanizates were investigated using the following test materials: isoprenyl, butadienyl, butadiene-methylstyryl, nitryl, butyl and chlorobutyl, acrylate, ethylenepropenyl, silicone and fluoro rubbers. It was shown that all unsaturated rubbers containing no vulcanizing agents, fillers or plasticizers could easily be vulcanized at 250°C and 500 MPa. The products obtained from such vulcanizates exhibited high heat stability and air-tight sealing ability. Using this method it was possible to decrease the use of vulcanizing agents or even to exclude them completely. This phenomenon was not observed with saturated or even partially saturated rubbers. Figures 2; references 5: 4 Russian, 1 Western.

[20-7813]

UDC 678.762.2-134.622:678.4.02

STUDY OF PROPERTIES OF TIRE COMPOSITIONS AND RESINS BASED ON SOLUBLE BUTADIENE-STYRENE RUBBERS DSSK-18 WITH VARIABLE STRUCTURES

Moscow KAUCHUK I REZINA in Russian No 9, Sep 83 (manuscript received 28 Apr 82)
pp 15-18

KUPERMAN, F. Ye., KANTOR, F. S., MASAGUTOVA, L. V. and NOVIKOV, S. V.,
Scientific Research Institute of Tire Industry

[Abstract] Soluble butadiene-styrene rubbers are obtained by anionic copolymerization using lithium organic initiators. The best combination of properties useful in tire rubber are shown in DSSK-18 copolymers containing 18% styrene, a minimum of 1.2 structure links and no block styrene. In order to improve technical properties of mixtures based on DSSK-18, the following aspects were studied: regulation of its molecular mass distribution (MMD), branching and localization of styrene microblocks at the terminals of the chain. It was shown that for DSSK it was possible to improve technological properties of the mixtures without lowering mechanical properties of the rubber by widening the MMD within certain limits and by simultaneously increasing the low and high molecular fractions at given values of \bar{M}_w or \bar{M}_v (average mass or viscosity M.W.) while maintaining \bar{M}_n higher than 100,000 (\bar{M}_n = average numerical M.W.). Branching of the polymer resulted in a sharp drop of the fluidity of the polymer and higher viscosity along with poorer technological properties due to a defective vulcanization process. Analogous end results were observed with introduction of terminal styrene blocks. Figures 3; references 7 (Russian).

[20-7813]

UDC 678.044.001.5:678.044.4

USE OF ZINC ISOBUTYLISOOCYLDITHIOPHOSPHATE IN LIGHT RUBBERS BASED ON SKI-3

Moscow KAUCHUK I REZINA in Russian No 9, Sep 83 (manuscript received 18 Nov 82)
pp 21-22

OVCHAROV, V. I., OMEL'CHENKO, R. Ya., BURMISTR, M. V., NEDAVA, L. V.
Dnepropetrovsk Institute of Chemical Technology imeni F. E. Dzerzhinskiy,
KF [expansion unknown] Scientific Research Institute of Rubber

[Abstract] In an attempt to improve properties of light rubbers and to intensify sulfur vulcanization in presence of zinc dialkyldithiophosphate (ZnDATP), the effect of nontoxic poly-p-xylene--N,N,N',N'-tetramethyl-p-xylylenediammonium chloride was investigated. It was established that cross-linking of high polyisoprene based mixtures with the system sulfur + ZnDATP + polyquaternary ammonium salts (PQAS) can be achieved without loss of their properties even at high vulcanization temperatures (160-170°C). Sulfur vulcanizates based on SKI-3 and ZnDATP + PQAS accelerator system were biologically inert. The modifying effect of PQAS was stronger than that of low molecular weight analogues. Products for veterinary application were developed from these vulcanizates. Figure 1; references 10: 9 Russian, 1 Western.
[20-7813]

UDC 658.4.065:629.11.012.551.3.004.2

ANALYSIS OF PERFORMANCE CRITERIA OF TUBELESS TIRES 400.00-57 ON 180 T
CAPACITY AUTOMATIC DUMP TRUCKS UNDER CONDITIONS EXISTING IN SOUTHERN
YAKUTSK COAL COMPLEX

Moscow KAUCHUK I REZINA in Russian No 9, Sep 83 (manuscript received 29 Sep 82)
pp 27-28

INDEYKIN, B. A., KLEVAYCHUK, N. V., NIKITINA, L. B. and SOLOV'YEVA, Z. M.,
Scientific Research Institute of Oversize Tires

[Abstract] Tires represent an important link in the system driver-vehicle-tire-road. The losses incurred due to tire wear and repairs represent 15% of the cost of transporting the load. Under the climatic conditions studied, the wear of heavy duty tires is increased due to weather and mineralogical conditions. According to theoretical calculations, these tires should last up to 60-70,000 km, but practically this goal is decreased markedly. One of the most critical factors affecting the wear of tires is the utilization regimen (load on the tires, air pressure, velocity of the vehicle during operations). A recommendation was made to perform routine temperature measurements of tires especially during dry summers, under conditions of rough roads extending over 2.5 km. Figures 2; references 2 (Russian).
[20-7813]

CSO: 1841

- END -